Alternative Materials for Sustainable Transportation

FINAL REPORT

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16. Abstract

A shortage of asphalt and polymers is creating opportunities for engineers to utilize alternative pavement materials. Three types of bio oil, untreated bio oil (UTB), treated bio oil (TB) and polymer-modified bio oil (PMB) were studied in this research. The research investigated the producing procedure of bio oil, the compatibility analysis between bio oil and petroleum-based asphalt, the rheological properties of asphalt binders modified and partially replaced by bio oil, the mechanical performances of asphalt mixtures modified by bio oil, and the lifecycle assessment and environmental impact of bioasphalt use. The main findings of the study include: 1) treated bio oil with low percent in the base asphalt can achieve appreciable or desirable stability with petroleum-based asphalt; 2) the virgin bioasphalt is softer than the traditional asphalt binder PG 58-28 but stiffer after RTFO aging because bio oil ages much faster than the traditional asphalt binder during mixing and compaction; 3) the binder test showed that the addition of bio oil is expected to increase the rutting performance while reduce the fatigue and low temperature performance; 4) the mixture test showed that (i) most of the bio oil modified asphalt mixtures had slightly higher rutting depth than the control asphalt mixture; (ii) the dynamic modulus of some of the bio oil modified asphalt mixture were lower than the control asphalt mixture; (iii) most of the bio oil modified asphalt mixtures had higher fatigue lives than the control asphalt mixture; (iv) the inconsistence of binder test results and mixture test results may be attributed to that the aging during the lab mixing and compaction was not as high as that in the RTFO aging simulation. 5) the implementation of Michigan wood bioasphalt is anticipated to reduce the emission but bring irritation on eyes and skins during the mixing and compaction; 6) the use of bioasphalt is expected to promote the job creation and regional growth.

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TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

EXCUTIVE SUMMARY

Currently, most of the asphalt binder materials used in HMA mixtures are from petroleum-based resources. Many researchers are striving to develop alternative materials that can be applied in the design and construction of asphalt pavements. Transportation policy makers are also increasingly considering the use of alternative materials to promote sustainable transportation. Bio oil which can be generated from wood waste and animal waste resources has attracted the attention of researchers. More research is needed to validate the use of these alternative paving materials and specify guidance for the application.

Even though some research strides have been made in developing bioasphalt for the asphalt pavement industry, they are not comprehensive enough to provide a guiding framework on the utilization of bioasphalt in both asphalt binder modifiers and pavements. In Michigan, the attempt to explore and use bioasphalt for advanced sustainable pavements has not been pursued. Therefore, this research will open up the field of bioasphalt development and utilization for durable asphalt transportation infrastructure in Michigan. It will also provide a solid research basis for other interesting bioasphalt research avenues in the State. Thus, the objectives of this study are: 1) literature review for the bio oil production as well as the physical and chemical properties of bio oil generated from forest-waste, swine waste and yard waste; 2) rheological performance evaluation of asphalt binders modified and partially replaced by bio oil generated from waste wood resources, including high temperature and low temperature evaluation, aging simulation and fatigue evaluation; 3) mechanical performance evaluation for bio oil modified asphalt mixture, including rutting performance, dynamic modulus, moisture susceptibility, fatigue evaluation; 4) life cycle evaluation and environmental impact of bioasphalt application; 5) recommendations for the application of bioasphalt in Michigan.

Three types of bio oil were studied in this study, including untreated bio oil (UTB), treated bio oil (TB) and polymer modified bio oil (PMB). The Automated Flocculation Titrimetry (AFT) test was conducted to study the compatibility of petroleum-based asphalt and bio oil generated from wood waste. Rotational Viscometer (RV), Dynamic Shear Rheometer (DSR), Bending Beam Rheometer (BBR), Rolling Thin Film Oven (RTFO) and Pressure Aging Vessel (PAV) test were conducted to characterize the rheological properties of asphalt binders modified and partially replaced by bio oil. Asphalt Pavement Analyzer (APA), Tensile Strength

Ratio (TSR), Four Point Beam Fatigue and Dynamic Modulus (E*) were conducted for the mechanical performance evaluation of asphalt mixtures modified by bio oil. The compatibility analysis results showed that: 1) treated bio oil (TB) which has limited water content can be a modifier with good stability for the petroleum-based asphalt binder; 2) with the addition of higher rates of TB in petroleum-based asphalt, conglomeration or assemblage of the asphaltenes will be reached with possible undesirable stiffening effects or loss of some elastic characteristics of the asphalt binder. The rheological test results showed that: 1) virgin bio oil is overall softer than the control asphalt binder PG 58-28; 2) bio oil aged much faster than the control asphalt binder; 3) the addition of bio oil into the control asphalt binder can enhance the rutting performance while sacrifice the fatigue and low temperature performance. The mechanical performance test results showed that: 1) the dynamic modulus (|E*|) of some UTB and TB modified asphalt mixtures were lower than that of the control asphalt mixture while the |E*| of PMB modified asphalt mixtures were higher than that of the control asphalt mixture; 2) the rutting depth of most of the bio oil modified asphalt mixtures were higher than that of the control asphalt mixture; 3) most of the bio oil modified asphalt mixtures had higher fatigue lives than the control asphalt mixture; 4) the control asphalt mixture and 5% bio oil modified asphalt mixture had higher TSR value than that of the 10% bio oil modified asphalt mixtures. The life cycle assessment and environmental impact discussions showed that: 1) the application of bio oil can reduce the CO, CO_2 and PM emission; 2) the acidity of the Michigan wood bio oil can cause irritation to the skin and eyes during the construction. Recommendations for some practices of bioapshalt use are presented in the report.

CHAPTER 1: INTRODUCTION

1.1 Background

The asphalt pavement industry in the United States is faced with increasing asphalt binder prices and decreasing reserves of crude petroleum. Skyrocketing asphalt market prices seek to erode the limited budget of the Michigan Department of Transportation for asphalt highway infrastructure development. Statistical facts and figures from the US Bureau of Labor Statistics report that asphalt binder and concrete prices have risen up to about 25% in the last five years with prices spiking in the 2008 construction season at more than a 300% increase in the price of asphalt cement in this same period. Market researchers speculate that the demand for asphalt products is likely to hit the 38.8 million ton mark in 2009. Such an astronomical demand will undoubtedly lead to unprecedented pressure on the petroleum resources of the United States.

In their quest to develop viable substitutes for petroleum-based materials like asphalt, transportation researchers and engineers have pursued notable research investigations into natural and artificial materials. Prominent among the waste materials that have immense potential are: a) industrial wastes such as cellulose waste, wood lignins, bottom ash and fly ash; b) municipal/domestic wastes such as scrap rubber and waste tires; and 3) mining wastes such as coal mine refuse. Of these waste materials, bio oil from cellulose waste presents the most environmentally-friendly, abundant and cost effective opportunity of utilizing alternative materials for asphalt infrastructure construction.

The range of cellulose biomass materials include agricultural and forestry waste products, municipal solid waste, and energy crops. These sources have been known to provide significant amounts of feedstock for the generation of bio fuels and its useful byproducts (Berton 1982; Pahl 2005; Perez 2005; Schubert 2006).

Scientific and technological advancements have made it more practicable and economical to convert cellulose biomass materials into ethanol for use as bio fuel with the potential of usurping crude oil for the energy needs of the United States. A joint research project conducted by the National Renewable Energy Laboratory (NREL) and the Department of Energy (DOE) indicated that saccharification and fermentation (SSF) process is the best option for producing ethanol with hemicellulose and lignin as quality co-products (Wyman 1992) .

As the demand for asphalt reaches astronomical proportions, the chief co-product of bio fuel generation – lignin presents transportation agencies with a material that has immense potential to become the single most important substitute for asphalt. Montague (Montague 2003) revealed that for a typical lignocellulose-biomass material, 10% to 30% by weight of essential lignin can be expected. This suggests a tremendous amount of lignin bio oil can be obtained with any available wood products and energy crops.

Past and current research investigations have shown that lignin, modified lignin and lignin products have immense potential for use in the asphalt industry. Significance among these studies was the work conducted by Gargulak and Lebo (Gargulak 1999) and Sundstrom et al. (Sundstrom 1983) who explored varied possible uses of lignin – asphalt binders, concrete admixtures, well drilling mud, dust control, vanillin production, and dispersants.

In the further development of bio oil as a non-petroleum based asphalt binder, Williams et al. (Williams 2008) have conducted research that utilizes processes named as fast pyrolysis and fractionation to extract lignin, modified lignin and lignin products. Key aspects of their research work involved: 1) a thorough insight into the pysio-chemical behavior of these lignin-based bio oils and; 2) the progressive refining of the bio oils produced to enhance their similarity as a substitute for asphalt binder.

Sundstrom and Klei(Sundstrom 1982) have also revealed that lignin from biomass had great potential for use as an asphalt extender. Furthermore, these lignins are produced in forms and structures related to the source of biomass, conversion process and conditions of preparation (Allen 1980). Researchers have also established the use of lignin as a biological polymer in retarding the aging (oxidation) of asphalt pavements (Dizhbite 2004; Bishara 2005; Ouyang 2006; McCready 2007). This function of lignin – a type of bio oil – serves to greatly prolong asphalt pavement life by reducing aging-related pavement failure such as thermal and fatigue cracking. In the latest research investigation conducted by McCready and Williams, lignin is found to have a profound effect on widening the performance grade range of asphalt binders.

1.2 Problem Statement

Transportation policy makers are increasingly considering the use of alternative materials to promote sustainable transportation. A shortage of asphalt and polymers is creating opportunities for engineers to utilize alternative pavement materials, such as bio oil produced from bio mass waste and forest products industry. Research is needed to validate the use of these alternative paving materials and specify guidance on their application. This constitutes an economic opportunity as well as a way to sustainably enhance the rheological and mechanical performance of asphalt.

1.3 Motivation for this Research

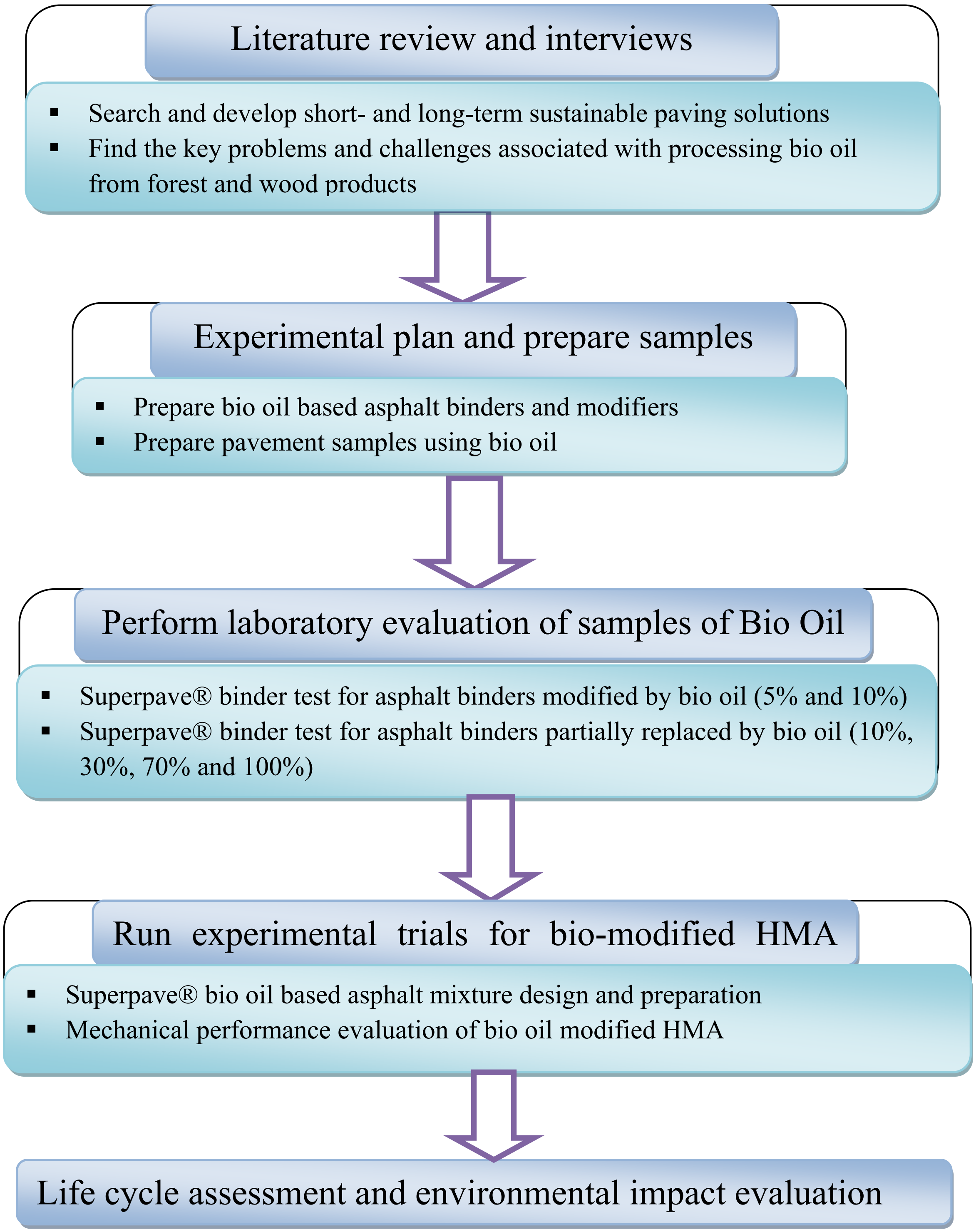
Even though some research strides have been made in developing bioasphalt for the asphalt pavement industry, they are not comprehensive enough to provide a guiding framework on the utilization of bioasphalt in both asphalt binder modifiers and pavements. In Michigan, the attempt to explore and use bioasphalt for advanced sustainable bioasphalt-modified pavements has not been pursued. Therefore, this research will open up the field of bioasphalt development and utilization for durable asphalt transportation infrastructure in Michigan. It will also provide a solid research basis for other interesting bioasphalt research avenues in the State.

Firstly, it is worth noting that there is no information regarding the pyrolysis of waste wood from different combined wood or forest tree types into bioasphalt materials. Typically, waste wood originating from sawmills come in different combined wood type blends in Michigan and it is relevant to study their feasibility as appropriate feed stock for bioasphalt production. Secondly, before the applications of combined waste wood bioasphalts into petroleum-based asphalt binders, it will be scientifically helpful to assess the solubility compatibility that occurs between the bioasphalt and petroleum-based asphalt binders. This has not been studied and thus research developments in such area will be most useful to the asphalt researchers and engineers. After the production of the bioasphalt from the different types of wood types, it will be pertinent to investigate the different chemical compounds and their respective functional groups in the bioasphalt. These functional groups translate into the different oxidation (aging) performance of the bioasphalt, which is not well understood. Conducting a comprehensive research study into how oxygen reactions occur within the bioasphalt functional groups will provide sufficient information on the rate of aging of the bioasphalt when it is used as modifiers or complete substitutes for petroleum-based asphalt binders. Full-scale research information on the rheological characteristics of combined wood-waste bio oil are needed for the design and construction of advanced asphalt paving mixes containing bio oil. In Michigan, low-temperature or thermal cracking has been one of the most problematic asphalt pavement distresses due to the mostly winter conditions. Therefore, an area that needs research attention is the performance behavior of bioasphalt-modified petroleum binder and pavements when subjected to the cold Michigan conditions. Another contentious issue that must be tackled is the bioasphalt response to moisture damage when used on the asphalt pavement road.

If bioasphalt is to be accepted as a partial replacement for typical petroleum-based asphalt binders in Michigan asphalt paving mixtures, the molecular to bulk-scale performance needs to be fully understood to ensure durable and sustainable performance satisfaction for the taxpayer.

1.4 Roadmap

The roadmap of this research is shown as follow:



1.5 Bioasphalt Feed Stock in Michigan

In developing bioasphalt from forest bio-resources, it is pertinent to study and understand the distribution, harvesting and productivity of notable biomass feed stocks in Michigan. This will provide a key framework on expanding the possibilities of converting the available bio-resources in Michigan into bioasphalt for the asphalt paving industry. The objectives of this section are: 1) conduct a literature review, telephone interviews and site visits to Michigan bio-resources; 2) define the qualitative and quantitative extent of these bio-resources in relation to their usefulness for bioasphalt development; 3) use geographic information tools to map the spatial distribution of the bio-resources in Michigan.

1.5.1 Woody Biomass Supply

According to available woody biomass literature, woody biomass-dependent industries can rely on about 19.3 million acres of timber land for processing and further development into end-use products (Shivan 2011). Figure 1-1 is a pie chart showing the ownership of the timberlands under the identifiable ownership groups.

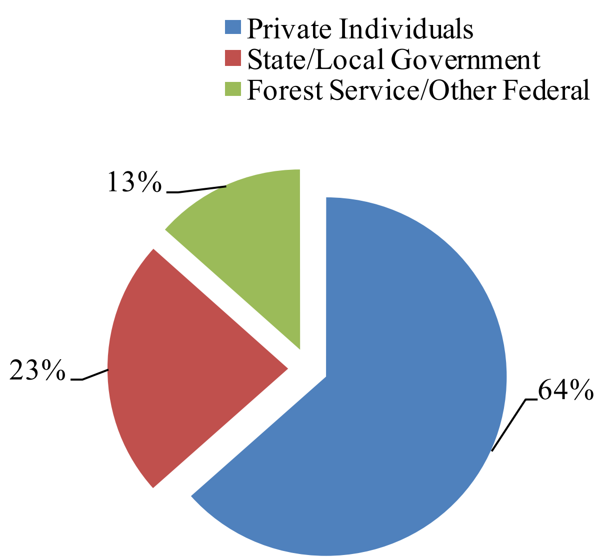


Figure 1-1: Percentage of Michigan timberland under each ownership group (Shivan 2011).

According to the Michigan Forest Inventory and Analysis, 385 million cubic feet of trees are available on Michigan timberland; considering the annual planting and removal of live trees under the different ownerships (Mueller). Logging residues remains after the trees have been felled and transported as timber logs on the timberlands. The paper, ethanol and power generating industries collect and process approximately 95.7 million cubic feet of logging residue for their work (Forest Service 2006). The Michigan Department of Natural Resources reported that about 315 primary and 1294 secondary manufacturing facilities exist in the State of Michigan while in 2007, Michigan primary mills were found to be working at approximately 71% of their maximum capacity (Mueller). Table 1-1 indicates by source, the volume of unused wood biomass in million cubic feet. One of the key findings from the Timber Product Output Resource is the fact that Michigan has 458.2 million cubic feet of unused annual growth and residues.

Table 1-1: Michigan Unused wood biomass volume, in million cubic feet, by source

Unused Biomass Resource							Total Available Vol.
Average annual net growth of live trees	Average annual removals of live trees	Unused growth	Average logging residue removed from MI	Logging residue that can be recovered after	Average mill residue	Unused mill residue	(Unused growth + recoverable logging residue + unused mill residue)
Million Cubic Feet							
763.2	**378.4**	**384.8**	**95.7**	**71.8**	**115.1**	**1.6**	**458.2**

Source: (Forest Service 2006)

1.5.2 Spatial Distribution of Bioasphalt Feed Stock in Michigan

This section deals with the spatial or geographic locations of biomasses in Michigan timberlands that can be processed into bioasphalt as a sustainable asphalt pavement transportation material. The Michigan Economic Development Corporation in collaboration with the Forest Department of Michigan Technological University has developed a useful computer software tool named the Forest Biomass Information System (FBIS) which was accessed and used.

1.5.3 Forest Biomass Information System (FBIS) methodology

The FBIS software tool contains an inventory of the spatial distribution of biomass species in Northern Lower or Upper Peninsula of Michigan. The software provides an interface where the Biomass Tools for analysis were selected. Since the analysis will cover a large land area for the spatial distribution, the "Select by Polygon" tool is utilized in-lieu of the 'Select by Point or Buffer". This 'Select by Polygon" tool was used to calculate the biomass contained within the

Upper Peninsula map appearing on the screen. A data log sheet or table showing the timberland species by ownership, and quantities within the defined polygon land area is finally provided. Figure 1-2 shows the FBIS polygon area used in the analysis and

Table 1-2 shows the biomass outputs generated for the various species. Based on the results, certain soft and hardwoods found readily available were selected for bioasphalt processing and their common and scientific names are provided in

Table 1-3.

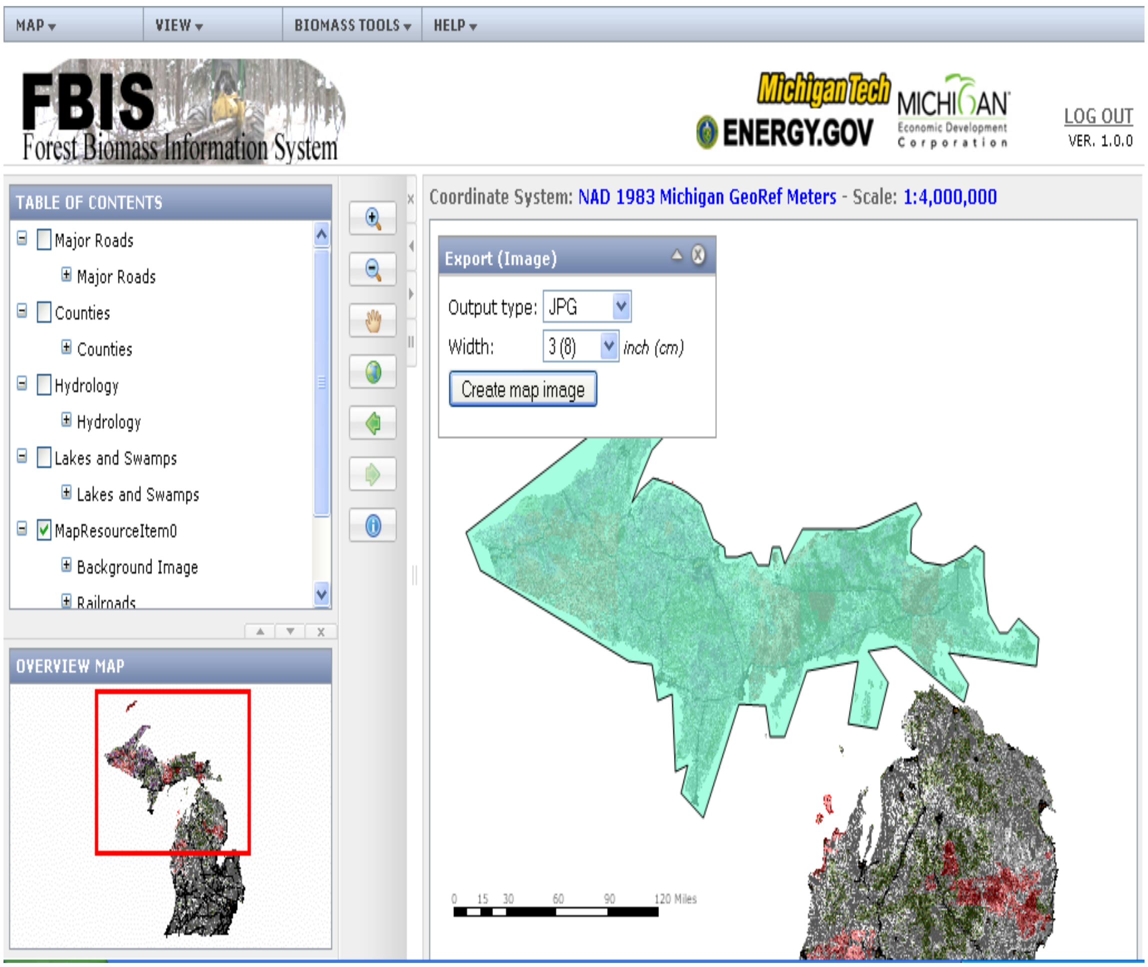


Figure 1-2: FBIS page showing the analysis area

Table 1-2: FBIS output showing the biomass spatial statistics

Forest Biomass Information System (FBIS) Results - Million Cubic Feet					
Ownership	**Hardwood Volume**	**Softwood Volume**	**Hardwood Growth**	**Softwood Growth**	**Hardwood Mortality**
Corporate	1720.88	889.25	27.81	16.00	12.68
State	1379.05	1217.31	22.52	22.42	11.58
Federal	1531.88	1104.09	23.43	19.91	13.26
NIPF	3230.33	2050.21	51.90	37.21	26.57
Forest Biomass Information System (FBIS) Results - Million Cubic Feet					
Ownership	**Softwood Mortality**	**Hardwood Removals**	**Softwood Removals**	**Hardwood Grow-Rem**	**Softwood Grow-Rem**
Corporate	7.71	19.37	4.29	7.93	11.53
State	9.29	14.76	5.95	7.39	16.27
Federal	9.87	15.37	5.78	7.67	13.95
NIPF	17.76	37.03	10.48	13.96	26.32

Table 1-3: Selected soft and hardwoods used as feedstock for bioasphalt production

Type of wood	**Common name**	Scientific name ((Piva 2010)
Softwood	1. Balsam fir 2. Jack pine 3. Shortleaf pine 4. Loblolly pine 5. Red pine 6. White pine 7. Scotch pine 8. Austrian pine	1. *Abiesbalsamea* 2. *Pinusbanksiana* 3. *Pinusechinata* 4. *Pinustaeda* 5. *Pinusresinosa* 6. *Pinusstrobus* 7. *Pinussylvestris* 8. *Pinusnigra*
Hardwood	1. Aspen/balsam poplar 2. Silver maple 3. Quaking aspen 4. American beech 5. Red maple 6. Bigtooth aspen	*1. Populusbalsamifera* *2. Acer saccharinum* *3. Populustremuloides* *4. Fagusgrandifolia* *5. Acer rubrum* *6. Populusgrandidentata*

1.5.4 Potential locations of bioasphalt refinery in Michigan's Lower Peninsula

In terms of ethanol production, biomass researchers have mapped out locations in Michigan's Upper Peninsula which are suitable for the construction and operation of an ethanol facility. These locations are provided in Table 1-4 (Zhang 2011) and the hypothesis is that such locations are also suitable for the construction and operation of pilot bioasphalt plants due to the similarity in feed stock material used, forest biomass – logging residue, wood mill waste chips and shavings.

Furthermore, list of potential ethanol bio refinery sites can also serve as strategic points for potential bioasphalt processing plants and their distances from the nearest biomass plants indicated in Table 1-4. The scope of this research only considered the Lower Peninsula of Michigan due to the timeline of the project and the available data as of the time this work was concluded.

Table 1-4: Potential Site for Pilot Bioasphalt Plants in Lower Peninsula of Michigan

City / Village	Distance to Nearest Biomass Power Plant (miles)
Manton city	11.19
Roscommon village	12.81
Kingsley village	23.86
Kalkaska village	23.94
Gaylord city	25.49
Clare city	33.97
West Branch city	35.29
Traverse City city	36.03
Boyne City city	41.24

* Source: (Zhang 2011)

1.6 Literature Review

1.6.1 Elemental analysis of bioasphalt fractions

The Carbon (C), Hydrogen (H) and Nitrogen (N) elemental investigations on the bioasphalt fractions was conducted. Table 1-5 shows the CHN composition in the various fractions analysed. It is evident that generally the carbon was the highest element followed by the hydrogen and then finally the nitrogen element. Since bioasphalt from combined wood type sources as an innovative alternative to petroleum-based asphalt binders, a comparative analysis was conducted between this bioasphalt and one from petroleum and swine waste sources (another innovative alternative bioasphalt being investigated. This comparison is provided in Table 1-6 from which it is evident that this bioasphalt from wood chips, sawdust and shavings has the least amounts of carbon, hydrogen and nitrogen elements. The relative amounts of carbon, hydrogen and nitrogen in petroleum-based asphalt has been known to affect the functional or polar group formations and it hypothesized that the same will apply to this wood-waste bioasphalt (Roberts 1996). However, the extent of this effect will be investigated in subsequent chapters of this dissertation. It is believed that this elemental difference will affect the chemical bonding behavior, morphological, rheological and bioasphalt-modified pavement mixture properties.

Table 1-5: Elemental analysis of bioasphalt fractions produced

Bioasphalt Fraction ID	Carbon %	Hydrogen %	Nitrogen %
1-20110712- SF1 Type I	59.54	6.68	0.37
1-20110712- SF2 Type I	58.22	6.60	0.21
1-20110718- SF1 Type II	58.71	6.58	0.18
1-20110718- SF2 Type II	58.88	6.64	0.29
Average	**58.83**	**6.62**	**0.27**

Table 1-6: Elemental composition of asphalt from different sources

Asphlat type	Carbon %	Hydrogen %	Nitrogen %
Petrdeum asphalt (fini et al. 2011)	81.600	11.600	0.800
Swine-waste bioasphalt (Fini et al. 2011)	71.600	9.800	4.500
Wood-waste bioasphalt	58.800	6.620	0.270
Comparative analysis	Wood-waste bioasphalt has least amounts of all 3 elements		

1.6.2 Moisture, solids and insolubles content

The relative amounts of moisture, solids and insoluble content in the final bioasphalt fractions are indicated in Table 1-7. Even though bioasphalts from corn stover, switch grass and oakwood were found to have water contents between 20 to 25%, this bioasphalt from combined wood waste sources had relatively low amounts of moisture; averagely about 5.27% (Williams 2009). Reduced moisture contents in bioasphalt are desirable to ensure consistent viscous behavior.

Table 1-7: Average material content of bioasphalt fractions

Bioasphalt Fraction ID	Moisture (%)	Solids %	Insolubles %
1-20110712- SF1 Type I	3.82	3.00	41.43
1-20110712- SF2 Type I	6.94	2.31	46.61
1-20110718- SF1 Type II	5.87	2.20	42.94
1-20110718- SF2 Type II	5.38	1.33	40.59
1-20110721- SF1 Type II	4.34	1.41	51.09
1-20110721- SF2 Type II	6.77	1.66	44.27
Average	**5.27**	**2.05**	**44.53**

1.6.3 GC-MS chemical compound investigations

Results of the gas chromatography-mass spectroscopy (GC-MS) analysis conducted on the bioasphalt are shown in Table 1-8. The dominating chemical functional compounds are:

- Levo
- 2, 6 dimethoxyphenol
- 2 methoxy 4 vinylphenol
- 2 methyl 1-2 cyclopentandione
- 4-allyl-2, 6 dimetoxyphenol

The phenol-related compounds present in the combined wood-waste blend of Aspen, Basswood, Red Maple, Balsam, Maple, Pine, Beech and Magnolia, are slightly acidic and are compounds based on benzene rings (Bortolomeazzi 2007). Furthermore, it was reported that this phenol-related groups have oxidation and thus aging properties (Bortolomeazzi 2007).

Table 1-8: Chemical compound analysis of bioasphalt fractions

Chemical compound	Percent weight of total			
	1-20110712		1-20110718	
	SF1 Type I	SF2 Type I	SF1 Type II	SF2 Type II
furfural	0.000	0.000	0.214	0.000
3 methyl-1-2 cyclopentandione	0.319	0.000	0.358	0.302
phenol	0.040	0.000	0.060	0.007
2 methoxyphenol	0.141	0.099	0.154	0.184
o-cresol	0.072	0.062	0.069	0.060
m-cresol	0.191	0.000	0.118	0.000
2 methoxy-4-methylphenol	0.142	0.107	0.275	0.180
p-cresol	0.000	0.069	0.067	0.000
2methoxy 4vinylphenol	0.489	0.375	0.541	0.372
eugenol	0.131	0.057	0.064	0.120
2,6 dimethoxyphenol	0.546	0.140	0.176	0.773
isogenol	0.331	0.280	0.346	0.818
levo	2.846	5.965	3.969	2.103
4 allyl-2,6 dimethoxyphenol	0.243	0.263	0.258	0.470
3,5 dimethoxy-4-hydrobenzaldehyde	0.199	0.218	0.207	0.920

1.6.4 Rheological performances of forest-waste bio oil

Some researchers have determined some interesting, but only preliminary physical, chemical and physical characteristics of bioasphalt produced from corn stover, switch grass and oak wood waste (Williams 2008). These worth mentioning findings are that: 1) the addition of this type of bioasphalt results in stiffening effect on petroleum-based asphalt binders; 2) The stiffening effect are dependent on the biomass source of bio-oil and amount of fractionated bio-oil; 3) the stiffening effect increases the high, intermediate and low critical temperatures of the asphalt-lignin blends, with the high temperatures increased more than the low temperatures. In terms of performance grade, the grade ranges in some combinations are increased by one grade (6ºC) and in other combinations no effects. Some of the characteristics of the bioasphalt to be anticipated are shown in Table 1-9.

The South Australian Roads and Traffic Authority (RTA) and the New South Wales counterparts have used the Australian GEO320 MRH molasses-based asphalt bitumen prototype developed in line marking road projects to good success. It passed the Australian Standard AS4049 Road Marking Standards (Australia™ 2009). It provided similar performance results comparable to Shell's CL320 residue bitumen which was used by the ARRB Transport Research in 2002. Preliminary results from this type of bioasphalt suggests that the GEO320 MRH bioasphalt holds great potential in resisting pavement distresses like fatigue, solvent, cracking, rutting, and skidding. Their results also showed that this kind of asphalt is compatible with glass spheres (balotini) for reflecting light for night time road safety. It is also compatible with recycled plastics and reclaimed tire rubber and the coloring system which Ecopave™ research has developed is resistant to wear and weathering. In compacting asphalt paving mixtures, GEO320 MRH gives the mixture low compaction properties, just like Warm Mix Asphalt.

Table 1-9: Characteristics of fractionated bio oil; adopted from (Williams 2008)

Property	Cond. 1	Cond. 2	Cond. 3	Cond. 4	ESP
Fraction of total oil (wt%)	6	22	37	15	20
pH	-	3.5	2.7	2.5	3.3
Viscosity @ 40°C (cSt)	Solid	149	2.2	2.6	543
Lignin Content (wt%)	High	32	5	2.6	50
Water Content (wt%)	Low	9.3	46	46	3.3
C / H / O Molar Ratio	1 / 12 / 0.5	1 /1.6/ 0.6	1 / 2.5 / 2	1 / 2.5 / 1.5	1/ 1.5 / 0.5

1.6.5 Rheological performance of swine-waste bioasphalt

This section of the literature review deals with collaborative research on swine-waste bioasphalt development conducted between Michigan Technological University and the North Carolina A & M University. The first part focuses on the swine-waste binder research led by North Carolina A & M with the aspect done by Michigan Technological University featured in the second part.

Preliminary characterization of swine-waste bioasphalt

Bioasphalt from swine waste or manure has been manufactured, refined and characterized quite recently as an innovative area (Fini 2010). At different rates of 2, 5 and 10% of swine waste bioasphalt added to standard PG 64-22 asphalt binder, the bio-modified PG 64-22 was prepared and characterized. A summary of the research work undertaken and the experimental results are shown in this section.

Preparation and characterization of swine bio-modified asphalt:

The swine based bio-binder was produced through a thermo-chemical liquefaction process. Past research has shown that the thermo-chemical process is capable of converting bio waste such as sewage sludge into bio oils (Williams and Besler 1992, Zahn et al., Zhang and Lei 1998, Ocfemia et al. 2006, Appell et al., 1971). Thermo-chemical liquefaction processing of the swine manure to bio-oil using a high pressure batch reactor followed by distillation was conducted based on the approach developed by Fini and his coworkers (Fini et al. 2011). A heavy-duty magnetic drive stirrer has been installed for the mixing. A type-J thermocouple has been fitted into the reactor to direct temperature measurements of the reaction media. A standard pressure gauge has been installed on the reactor head. A temperature controller is used to control the temperature of the reactor (Fini et al. 2011). During the process, swine waste was degraded by heating in the absence of oxygen to provide a complex volatile phase, a carbonaceous char and the bioasphalt. The bioasphalt was then processed to be refined of any physical contaminants to produce bio-binder. The bio-binder is then mixed with the PG 64-22 asphalt binder at the rate of 5% by total weight using a mechanical shear device.

The experimental program was designed to cover a comprehensive range of asphalt binder specification tests to determine the low, intermediate and high temperature rheological properties and performance of both the control PG 64-22 binder and the modified binder. The relevant unmodified (PG 64-22) and modified (5% BMB) samples prepared and tested are unaged, RTFO-aged and PAV-aged. It was shown that bio-binder has a high level of nitrogen relative to typical asphalt binder but a very close ratio of carbon to hydrogen content. The carbon-13 NMR spectrum indicated that the bio-binder is comprised mainly of carbons in straight chainaliphatic compounds. The 1H NMR spectrum showed presence of olefins and alcohols; this was also found by GCMS. The specific gravity of bio-binder (1.01) was found to be close to that of asphalt binder (1.03). It was also shown that both materials have similar chemical composition, water and ash content. In terms of elemental comparisons, the PG 64-22 has about 81.6% carbon by percent weight of total elements while the bio-binder has about 72.6%. For hydrogen, the PG 64-22 has 110.8% while the bio-binder has 9.8%. Furthermore, the nitrogen and oxygen contents in the PG 64-22 were 0.8% and 0.9%, respectively, while the bio-binder had 4.5% and 13.2% of the nitrogen and oxygen, respectively. To further characterize the swine-waste bioasphalt, the rotational viscosity, dynamic shear modulus and asphalt binder thermal cracking critical temperature was evaluated.

Experimental results on 2, 5 and 10% swine bio-modified asphalt:

The rotational viscosity, dynamic shear modulus and the asphalt binder cracking behavior are shown in Figure 1-4 to Figure 1-6 (Fini 2010). It can be seen from Figure 1-4 that progressively, as the rate of swine-waste amount increases in the PG 64-22 petroleum-based asphalt, the rotational viscosity behavior decreases between the temperature range 100°C, 110°C, 115°C and 135°C. This implies the use of swine waste bioasphalt can induced less viscous behavior which is desirable for storage and mixing performance. According to Figure 1-4, the dynamic complex modulus decreased with increasing rates of the swine waste asphalt. This validated the earlier rotational viscosity result since for a decreasing viscosity trend, the corresponding dynamic shear modulus or stiffness is also expected to decrease. The thermal cracking temperature behavior as established by the asphalt binder cracking device (ABCD) is presented in Figure 1-5. It is seen that adding swine-waste bioasphalt to petroleum-based asphalt causes the resultant hybrid asphalt binder to crack at lower temperatures and thus better low-temperature cracking performance. This aspect of the research was done by the research team at the Michigan Technological University Transportation Materials Research Laboratory.

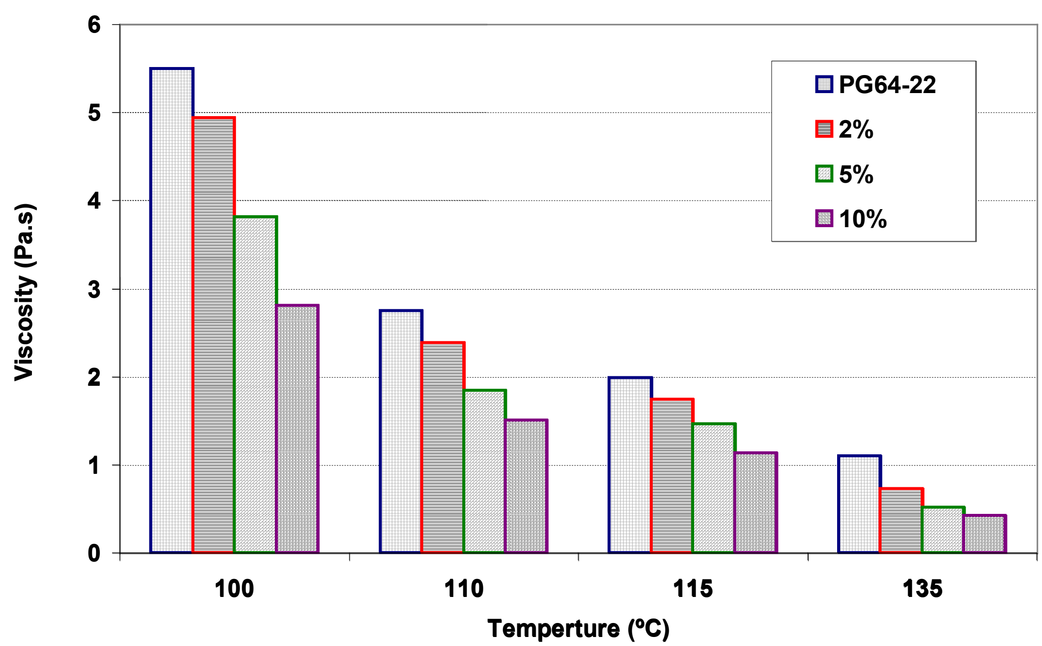


Figure 1-3: Effect of swine waste binder on petroleum-based asphalt (Fini 2010)

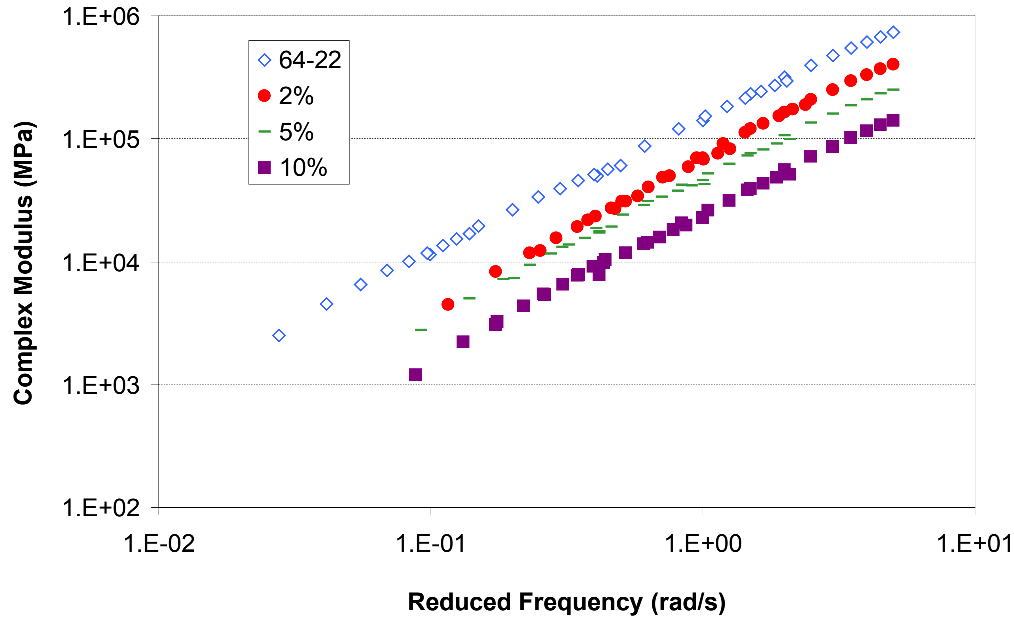


Figure 1-4: Effect of swine waste binder on petroleum-based asphalt (Fini 2010)

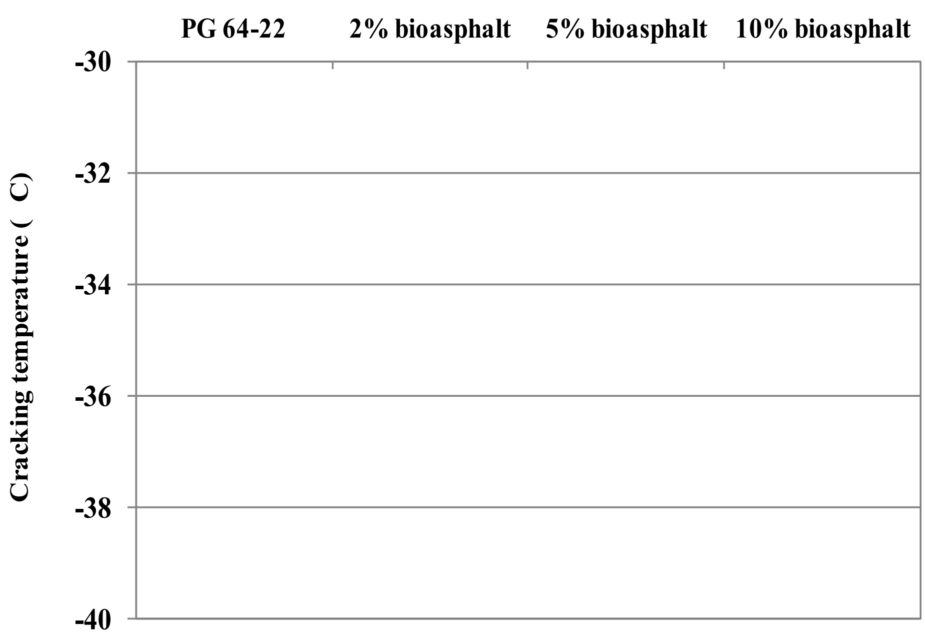


Figure 1-5: ABCD cracking temperature, t_{cr}, behavior of swine binder modified asphalt (Fini 2010; You 2011)

Advanced characterization of swine-waste bioasphalt

At Michigan technological University, work has been done on using the Fourier Transform Infra-red Spectroscopy (FTIR) to investigate the aging and morphological behavior of petroleum-based asphalt containing swine-waste asphalt binder. Prior to that, the bending beam rheometer (BBR) had been used to characterize the thermal cracking stiffness behavior at -18°C and -24°C. The results of the thermal cracking performance are shown in Figure 1-6. After adding 5% swine-waste bioasphalt to the PG 64-22, the temperature grade dropped from a PG -22°C to a PG -28°C. The 5% BMB, however, failed the Superpave™ specification standards at test temperature of -24°C and its corresponding PG grade of -34ºC. This trend reveals that bio-binder from swine waste can potentially enhance the thermal cracking or low-temperature performance of traditional asphalt by lowering the creep stiffness; which is highly desirable.

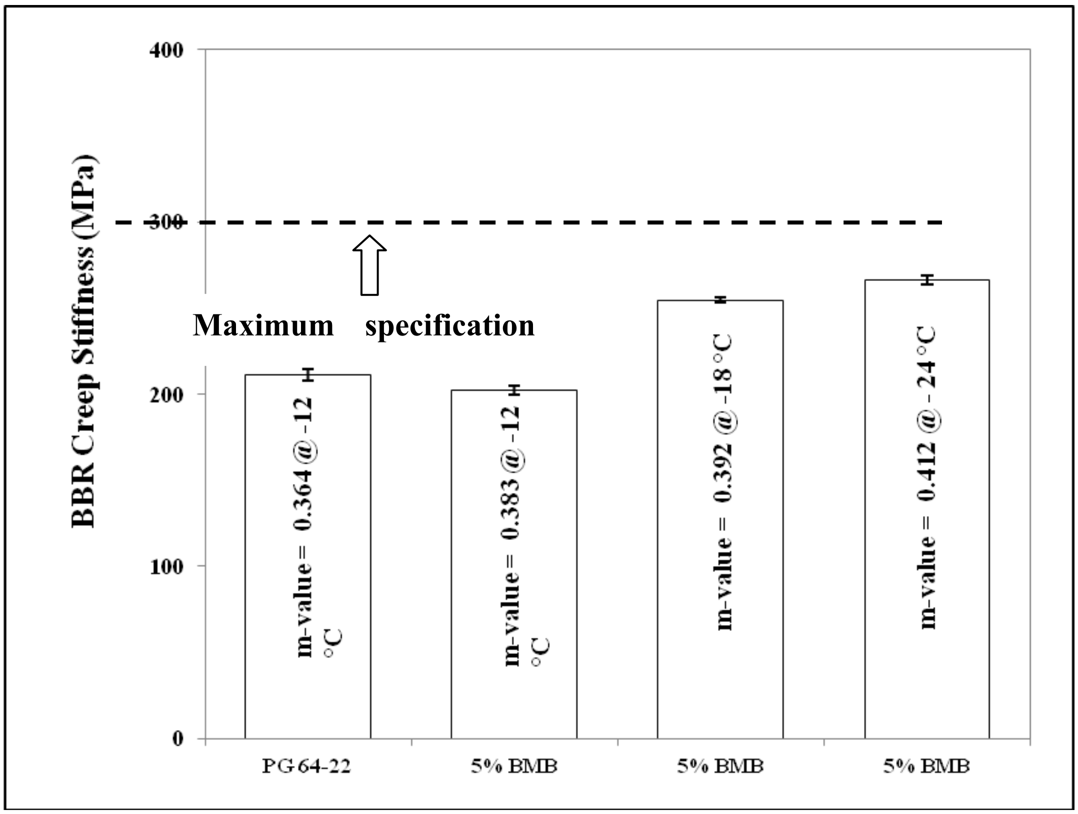


Figure 1-6: Bar chart plots on the BBR creep stiffness behavior of samples

1.6.6 Rheological performance of yard waste bioasphalt

Researchers at Peking University in Beijing, China, (Barras 2008) have developed a method for the characterization of the lignin components in saw dust and yard waste. Their method proved that the lignin has carbon-oxygen-carbon bonds that hold together smaller hydrocarbon chains. The intermediary products are alkanes and alcohols in which the breakdown of C-O-C bonds occurs to unlock the smaller hydrocarbons. They have further established that within the smaller hydrocarbons are C-O-C bonds that need to be preserved if the optimum yield of bio oil or bio asphalt will be realized from yard waste. Therefore, the chief approach to realize bioasphalt resources from saw dust and other yard waste is to design a balanced chain breaking and maintenance procedure. This is achieved by destroying or breaking the C-O-C bonds between chains and keeping intact the chains within the chains.

The bio oils from saw dust production technique developed in China created three principal components: 1) alkanes with eight or nine carbon atoms suitable for gasoline; 2) alkanes with 12 to 18 carbons for use in diesel; 3) and methanol. Asphalt engineers are obviously interested in the alkanes with 12 to 18 carbons since further processing on it can lead to bioasphalt.

Yard waste bioasphalt has not entered the phase where the manufactured bioasphalt resource will be evaluated for its laboratory and field performance suitability in asphalt pavements. Such a reason is one of the driving forces behind the commencement and successful completion of this research. Bioasphalt research at the laboratory and field testing stages is yet to commence since the production is still in the infantile stages.

CHAPTER 2: EXPERIMENTAL PLAN AND SAMPLE PREPARATION

2.1 Experimental Plan

The experimental plan of this study mainly includes: 1) compatibility and morphological performance evaluation of asphalt binders modified by bio oils; 2) rheological property evaluation of asphalt binders modified bio oils; 3) Mechanical performance evaluation of HMA mixtures modified by bio oils.

2.1.1 Compatibility and morphological performance evaluation of asphalt binders modified by bio oils

The main experimental plan in this section can be divided into two parts:

1) Using the Automated Flocculation Titrimetry (AFT) to investigate physio-chemical, morphological and compatibility properties of the bioasphalt binders. For the petroleum-based asphalt binder made up of asphaltene and maltene, it is pertinent that the distribution and precipitation of the asphaltene fractions out of the maltene solvent be established when the bio oil is added to the conventional asphalt. Furthermore, this research establishes the degree of compatibility and solubility between the petroleum-based asphalt binder and the bio oil.
2) Utilize the FTIR to characterize the chemical functional groups and the aging indices of bioasphalt binders after aging. Knowledge of the prevailing functional groups will allow for the understanding of some of the possible chemical reactions that will impact the storage, mixing, compaction and in-service morphological behavior of the bio oil modifier within the asphalt binder matrix.

2.1.2 Rheological Property Characterization of Asphalt Binders Modified by Bio Oil

The main task of this section is to characterize the rheological properties of asphalt binders modified by bio oil. Superpave^{TM} binder test is conducted on the control binder, 5% and 10% bio oil modified asphalt binders. These tests and the functions are: Rotational Viscosity (RV) test to determine the mixing and compaction temperature of asphalt binders; Rolling Thin Film Oven (RTFO) test to simulate the short-term aging of asphalt binders during the construction period; Pressure Aging Vessel (PAV) test to simulate the long-term aging of asphalt binders during the service life; Dynamic Shear Rheometer (DSR) test for virgin and RTFO aged asphalt binders to evaluate the high temperature performance of asphalt binders and mixtures; DSR test for PAV aged asphalt binders to evaluate the fatigue performances of asphalt mixtures during the service life; Bending Beam Rheometer (BBR) test to evaluate the low temperature performances of asphalt binders and mixtures.

Three different types of bio oils, untreated bio oil (UTB), treated bio oil (TB) and polymer modified bio oil (PMB) are investigated in this study. The detailed test plan is shown in Table 2-1.

Table 2-1: Rheological test plan for bio oil modified asphalt binders

Test Equipment	Control	UTB		TB		PMB	
		5%	10%	5%	10%	5%	10%
RV test	XXX	XXX	XXX	XXX	XXX	XXX	XXX
DSR for virgin binders	XXX	XXX	XXX	XXX	XXX	XXX	XXX
DSR for RTFO aged binders	XXX	XXX	XXX	XXX	XXX	XXX	XXX
DSR for PAV aged binders	XXX	XXX	XXX	XXX	XXX	XXX	XXX
RTFO for virgin	XXX	XXX	XXX	XXX	XXX	XXX	XXX
PAV test	XXX	XXX	XXX	XXX	XXX	XXX	XXX
BBR test	XXX	XXX	XXX	XXX	XXX	XXX	XXX

*note: X means one replicate

2.1.3 Rheological Property Characterization of Asphalt Binders Partially Replaced by Bio Oil

In this section, the bio oil serves as extenders in the base asphalt binders. Rheological properties of 10%, 30% and 70% of bio oil blended asphalt binders are studied. Preliminary research showed that if using the standard RTFO and PAV aging process, the bio oil would be over aged, a modified RTFO and PAV aging process was proposed (Metwally and Williams 2010). The difference of the modified and standard RTFO test lies in the aging time and aging temperature, which is reduced to 20 minutes at 120°C from 85 minutes at 163°C respectively. Because the tests in this part deals with high percentage of bio oil blended asphalt binders, the aging of the mixed asphalt binders would be very high. As a result, both the RTFO and PAV test are adopted as the modified procedure as mentioned above. Other Superpave^{TM} binder tests including RV test, DSR test and BBR test follow the standard test procedures. The detailed test plan is listed as Table 2-2.

Table 2-2: Rheological test plan for asphalt binders partially replaced by bio oils

Test equipment	Control	TB			TB			PMB		
		10%	30%	70%	10%	30%	70%	10%	30%	70%
RV test	XXX	XXX	XXX	XXX	XXX	XXX	XXX	XXX	XXX	XXX
RTFO test	XXX	XXX	XXX	XXX	XXX	XXX	XXX	XXX	XXX	XXX
DSR test	XXX	XXX	XXX	XXX	XXX	XXX	XXX	XXX	XXX	XXX
PAV test	XXX	XXX	XXX	XXX	XXX	XXX	XXX	XXX	XXX	XXX
BBR test	XXX	XXX	XXX	XXX	XXX	XXX	XXX	XXX	XXX	XXX

*note: X means one replicate

2.1.4 Mechanical Performance Evaluation of Hot Mix Asphalt Modified by Bio Oil

In this part, the mechanical performances of HMA mixture modified by bio oils are evaluated. The related performance tests are: Asphalt Pavement Analyzer (APA) test and Flow Number (FN) test for rutting resistance evaluation; Dynamic Modulus (E*) test for the stiffness property evaluation; Indirect Tensile (IDT) test for the tensile strength evaluation; Tensile Strength Ratio (TSR) test for moisture susceptibility evaluation; beam fatigue test for fatigue life evaluation.

Considering that high percentage of bio oil blended asphalt mixture would use a lot of bio oils beyond of the research team's storage, only low percentage of bio oil containing HMA mixture are studied. The detailed test plan is listed as Table 2-3.

Table 2-3: Mechanical performance test plan for bio oil modified HMA mixtures

Test equipment	Control	UTB		TB		PMB	
		5%	10%	5%	10%	5%	10%
APA test	XXX	XXX	XXX	XXX	XXX	XXX	XXX
E* test	XXX	XXX	XXX	XXX	XXX	XXX	XXX
IDT test	XXX	XXX	XXX	XXX	XXX	XXX	XXX
TSR test	XXX	XXX	XXX	XXX	XXX	XXX	XXX
Beam Fatigue test	XXX	XXX	XXX	XXX	XXX	XXX	XXX
FN test	XXX	XXX	XXX	XXX	XXX	XXX	XXX

*note: X means one replicate

2.2 Sample Preparation

2.2.1 Preparation of bio oil

This section describes the preparation and fast pyrolysis process employed for the manufacture of the bioasphalt from the waste wood chips and shavings. The fast pyrolysis process is defined as a process whereby the waste wood chips and shavings were rapidly heated in a vacuum thereby decomposing them into solid bio-char, vapors and aerosols (Mohan 2006).

The pyrolysis process was categorized into four aspects according to past work by Mohan (Mohan 2006):

- Drying the wood waste and shavings at 110 °C for 24 hours;
- Pyrolysing the wood waste and shavings in the region of 425-500 °C;
- Vaporizing the pyrolysed products at residence times less than 2 seconds;
- Rapid cooling of pyrolysis vapors and aerosols to produce bio-oils.

Figure 2-1 shows a schematic diagram of the 25KWt fast pyrolysis plant which has a fluidized-bed reactor. The pyrolysis plant used was developed at the Iowa State University Center for Sustainable Energy Technologies (CSET) with the processing capacity of between 6 to 10 kg/h of the waste wood chips, shavings and sawdust. The functions components of this reacting plant are a 16.2 cm diameter fluidized bed reactor, burner to externally heat the reactor, a two-stage auger to feed the solid, 2 cyclones to remove particulate matter, vapor-condensing system consisting of four condensers and an electrostatic precipitator, a fractionation condenser for separating the bioasphalt into different fractions.

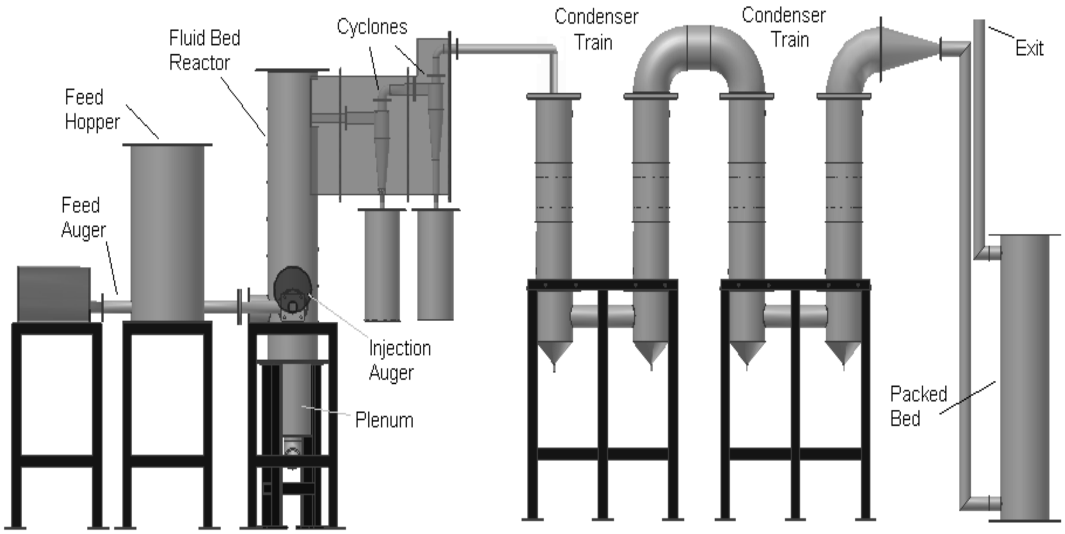


Figure 2-1: A schematic of the fluidized bed fast pyrolysis unit used in this research

2.2.2 Preparation of bio oil based asphalt binders

- ***Mixing condition of bio oil and base asphalt***

Before the mixing of bio oil and base asphalt, the base asphalt is heated to about 120°C. Since the bio oil is stored in plastic bottles and it's not proper to heat it in the oven, a water bath is used to take out the bio oil from the bottle. Thus, the temperature to heat the bio oil samples is about 90 to 100°C. After the heating, the bio oil and base asphalt are mixed with the designed fractions. The mixing temperature for bio oil and base asphalt are 90°C and 120°C respectively.

- ***High shear mixing of base asphalt and bio oil***

The mixing procedure of base asphalt PG 58-28 and bio oil was conducted by the high speed mechanical shearing equipment. During the mixing, the screw of the mixer rotated with a high speed, which causes a whirl flow inside the asphalt binder liquid. The whirl flow made the base asphalt and bio oil mix well. The mixing condition was 5000rpm at 110°C for 15 minutes. The higher speed can make stronger whirl flow, which is beneficial for the uniformly mixing of the two components. The higher the mixing temperature is, the easier is the mixing process because of the higher fluidity. However, the high temperature may cause a significant aging during the mixing, which will have great influence on the following testing. Williams (2009) pointed that 120°C is a convenient mixing temperature for bio oil. The research team found the mixing can also be conducted very well under 110°C, so 110°C was selected as the mixing temperature. To avoid the aging caused by long mixing time but make sure the mixing is very well, the mixing time was determined as 15 minutes.

2.2.3 Preparation of asphalt mixture samples containing bio oil

The mixture samples of asphalt pavement analyzer (APA) test, Indirect tensile strength (IDT) test, tensile strength ratio (TSR) test, dynamic modulus (E*) test and flow number (FN) test are prepared by the Superpave^{TM} Gyratory Compactor (SGC) for 86 gyrations. Three asphalt mixture samples with different binder contents are compacted first and the rice test is conducted to determine the bulk specific gravity (Gmb) and the maximum theoretical specific gravity (Gmm). Based on the tested Gmm and Gmb, the optimum binder content is determined.

- ***APA test***

The standard test procedure for the APA test is according to AASHTO TP 63. The mixture sample tested in the APA test is cylinder with 150mm in diameter and 75mm in height. The air voids of the sample are 4%.

- ***Dynamic shear modulus (E*) and FN test***

The recommended specimen size for E* test is 100mm in diameter by 200mm high, it may be possible to use smaller specimen heights with success. The specimen size prepared in this study is 100mm in diameter by about 150mm high compacted by the SGC to a 4% air voids. The sample preparation of FN test is the same as that of the E* test.

- ***Indirect Tensile Strength (IDT) and Tensile Strength Ratio (TSR) test***

The sample preparations for IDT test and TSR test are in accordance with AASHTO TP 9 and AASHTO T 283. The sample size is 100mm in diameter by 63.5±1.5mm high. The specimen is compacted to a targeted 7% air void.

CHAPTER 3: MOLECULAR-SCALE FLOCCULATION BETWEEN PETROLEUM-BASED ASPHALT AND WOOD-WASTE BIOASPHALT

3.1 Introduction

The objectives of the research in this chapter are to :1)investigate the precipitation behavior of petroleum-based asphalt modified with the wood-waste bioasphalt 2) characterize the physio-chemical aging performance of pure wood waste bioasphalt, unmodified petroleum-based asphalt and bio oil modified petroleum-based asphalt using the Fourier Transform Infra-red Spectroscopy (FTIR); 3) investigate the precipitation behavior of petroleum-based asphalt modified with the wood-waste bioasphalt using the Automated Flocculation Titrimetry (AFT).

3.2 Research Methodology

Firstly, the methodology for this research involves the use of the Fourier Transform Infra-red Spectroscopy (FTIR) and the Automated Flocculation Titrimetry (AFT) to investigate physio-chemical, morphological and compatibility properties.

Secondly, the mixing/compaction and in-service aging performance of the bio oil modified petroleum-based asphalt are simulated using the rolling thin film and pressure aging vessel, respectively. Immediately following the aging simulation is the utilization of the FTIR to characterize the chemical functional groups and then the aging indices.

Thirdly, in order to evaluate the flocculation behavior of the chemical molecules of the bio oil modified asphalt binder, the automated flocculation titrimetry approach is employed. It involves determining how the higher molecular asphaltene fractions in the petroleum-based asphalt will either conglomerate or disperse in the lower molecular maltene fractions with the presence of the bioasphalt, which is viewed as a new "*chemical*" that has been added.

3.2.1 Scope of materials

A traditional asphalt binder of Superpave™ Performance Grade (PG) 58-28 used for a road project in Spread Eagle, Michigan was selected as the base binder. The PG 58-28 asphalt binder is modified with 2% of treated bio oil (TB). The materials used and their description is provided in Table 3-1.

Table 3-1: Flocculation Titrimetry Test Specimens

Treated Bio oil (%)	Specimen ID Code	Number of Replicates
0% (Control)	AFT MB.0	XXX
2%	AFT MB.2	XXX

3.2.2 Experimental Program

- **Preparation and GC-MS characterization of bio-modified asphalt binder**

The PG 58-28 asphalt binder was modified with the bio oil at the rate of 2, 5 and 10% using a high speed blender operated at 1200 revs/min. about 120 °C for 10 minutes to achieve uniform blending. In order to characterize the chemical compounds present in the bioasphalt, the Gas Chromatography-Mass Spectroscopy (GC-MS) technique was utilized.

- **Oxidation hardening (Aging) simulation**

The Rolling thin Film Oven (RTFO) and Pressure Aging Vessel (PAV) aging simulation were conducted on the control PG 58-28 asphalt binder. Also, the same aging testing was done on 2%, 5% and 10% bio-modified PG 58-28 asphalt binder. The RTFO and PAV oxidation simulation was undertaken following the ASTM 2872 (AASHTO T 240) and ASTM D 6521 (AASHTO R 28), respectively. While the RTFO aging simulated the mixing and compaction hardening performance (short-term aging), the PAV aging simulated the in-service hardening (long-term aging) performance.

- **Fourier Tranform Infra-red (FTIR) characterization**

Fourier Transform Infra-red Spectroscopy (FTIR) investigations are conducted on the control, untreated and treated bio oil to characterize: 1) the chemical functional groups present and; 2) the oxidation hardening (aging) performance. The FTIR research was done on the unaged PG 58-28 asphalt binder, untreated and treated bioasphalt specimens. The chemical and morphological behavior of the bio oil modified specimens using the FTIR was undertaken on the control PG 58-28 asphalt binder (0% bioasphalt), 2%, 5%, 10% and 100% bioasphalt by weight of base binder using a Jasco FTIR-4200 spectrometer. To prepare the test specimens, the PG 58-28 asphalt binder was heated to 120 °C until workable enough to be poured. 2%, 5% and 10% by weight of base binder was mixed into the workable PG 58-28 binder and homogenously mixed with a mechanical shear mixer at 1500 revs/min. With the aid of a smooth brush, the liquefied asphalt binders were then spread on silicon slides of dimensions 1.5-cm long x 1.0-cm breadth x 0.5-mm thickness. For optimum FTIR spectra results, a maximum asphalt coating thickness of about 1mm was achieved. The FTIR used was a Jasco FT-IR-4200 spectrometer, with 32 numbers of scan and the resolution of 4 cm^{-1}.

- **Automated Flocculation Titrimetry (AFT) characterization**

Two different types of materials were used during the AFT research investigations. These materials were the PG 58-28 control and 2% treated bioasphalt modified PG 58-28 samples. The asphaltene content in petroleum-based asphalt binders is defined as the fraction insoluble in n-heptane but soluble in toluene (Pfeiffer 1940). This property finds use in the automated flocculation titrimetry research. The control and 2% treated bioasphalt modified PG 58-28 petroleum-based asphalt were first dissolved in toluene organic compound at various concentrations and titrated with iso-octane or n-heptane at controlled temperatures between 20-100°C to determine the point of flocculation (asphaltene precipitation) and thus the Heithaus compatibility parameters. The test data was used to estimate the colloidal stability of the bioasphalt –petroleum asphalt cross blends. Figure 3-1 shows a schematic of the automated flocculation set-up used in the research investigations.

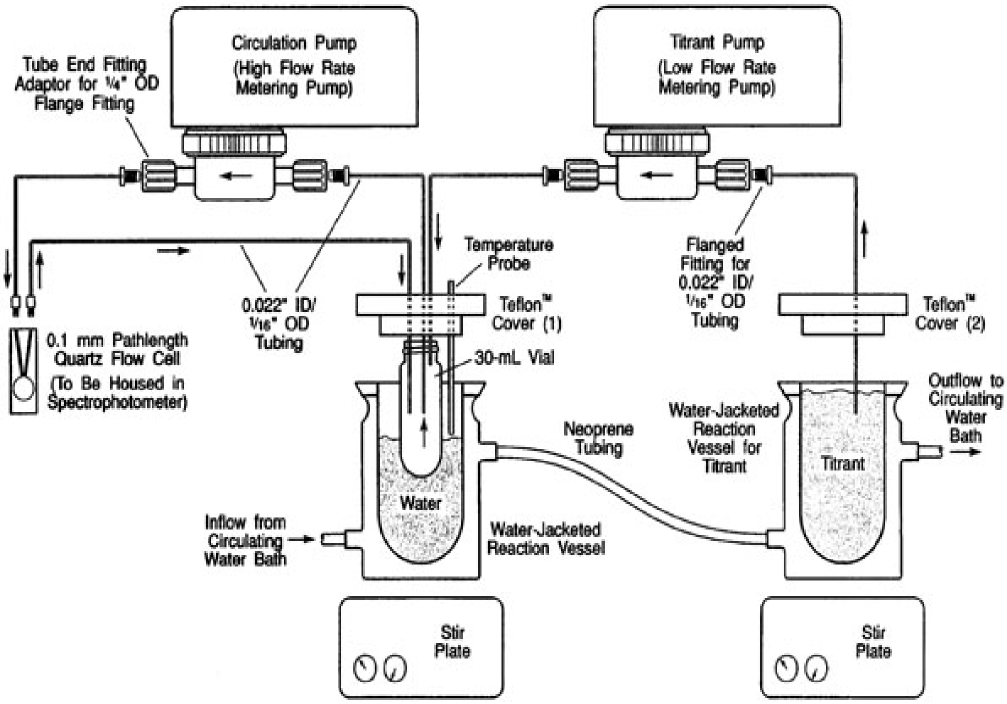


Figure 3-1: A schematic of the Automated Flocculation Titrimetry (AFT) (Koehler 2011)

3.2.3 Results and Discussion

- ***Physical and chemical composition***

The acidity of the processed bioasphalt was found to be around 2.7 on the pH scale. Furthermore, the Carbon-Hydrogen-Nitrogen content was found to be 58.83, 6.62 and 0.27 %, respectively. In Table 1, a comparison is made between typical petroleum-based asphalt, swine waste asphalt and this wood-waste bioasphalt. From Table 3-2, it is evident that this bioasphalt from Aspen, Basswood, Red Maple, Balsam, Maple, Pine, Beech and Magnolia has the least amounts of Carbon, Hydrogen and Nitrogen elements. The effect of this difference in elemental composition is hypothesized to potentially influence the chemical compound composition, morphological and oxidative hardening behavior which was investigated in this research. The moisture content of the bioasphalt immediately from the pyrolysis plant source was found to be averagely 5.3%. It is this water content that is reduced down to approximately 1% after the preheating (cooking) for 2 hours at 120 °C.

Table 3-2: Elemental composition of asphalt from different sources

Asphalt Type/Source	C	H	N
Petroleum-based asphalt (Fini et al. 2011)	18.60	11.60	0.80
Swine-waste asphalt (Fini et al. 2011)	11.60	9.80	4.50
Wood-waste bioasphalt	58.80	6.62	0.27

Results of the gas chromatography-mass spectroscopy (GC-MS) analysis conducted on the levo, 2, 6 dimethoxyphenol, 2 methoxy 4 vinylphenol, 2 methoxy-4-methylphenol, 2 methoxyphenol, 2 methyl 1-2 cyclopentandione, 4-allyl-2, 6 dimetoxyphenol, 3 methyl-1-2 cyclopentandione, 3, 5, dimethoxy-4-hydrobenzaldehyde, furfural, phenol, o-cresol, m-cresol, p-cresol, eugenol and isogenol. It is believed that the phenol-related compounds present in the bioasphalt generated from wood-waste blend of Aspen, Basswood, Red Maple, Balsam, Maple, Pine, Beech and Magnolia gives it the slightly acidic nature and the phenols are compounds based on benzene rings. This is in agreement with research conducted by Bortolomeazzi(Bortolomeazzi 2007). Bortolomeazzi further reported that this phenol-related groups have oxidation and thus aging properties (Bortolomeazzi 2007).

- ***Functional groups and physiochemical properties***

FTIR spectra were generated for the pure PG 52-28 control binder, untreated and treated bioasphalt specimens. The first part of the FTIR is the graphical representation of spectra as a graph of absorbance against wavenumber in cm^{-1}. The absorbance spectra for the control PG 58-28 asphalt binder from petroleum source, treated and untreated bioasphalts are overlayed or superimposed on each other to understand the relative variations in the functional groups of the three different materials. In Figure 3-2, the superimposed FTIR spectra are provided for the pure (unmodified) PG 58-28, 100% untreated and treated bioasphalt. Firstly, it can be observed that the absorbance spectra trends for the control petroleum asphalt on one hand and the bioasphalt samples (untreated and treated) on the other are different. However, the two bioasphalt samples, under treated and untreated conditions have similar spectra since they are from the same combined wood waste source. An attempt is made to characterize the functional groups from the absorbance peaks generated for these samples. The functional groups identified from the spectra for the conventional petroleum-based asphalt binder, PG 58-28, is provided in Table 3-3. Furthermore, functional groups of the treated and untreated bioasphalt samples and some expected chemical behaviors provided in Table 3.

Table 3-3: Functional groups identified for the control PG 58-28 petroleum-based asphalt

Functional Group	Absorption wave number (cm^{-1})	Class of compound
C-H in plane bending	700 - 900	Aromatic compounds
S=O	997 - 1043	Sulphoxide
CH_3	1372 and 1445	Aliphatic compounds
C=C ring stretch	1595	Aromatic compounds
CH_2 (methylene) and CH_3 (methyl)	2803 - 3066	Aliphatic compounds

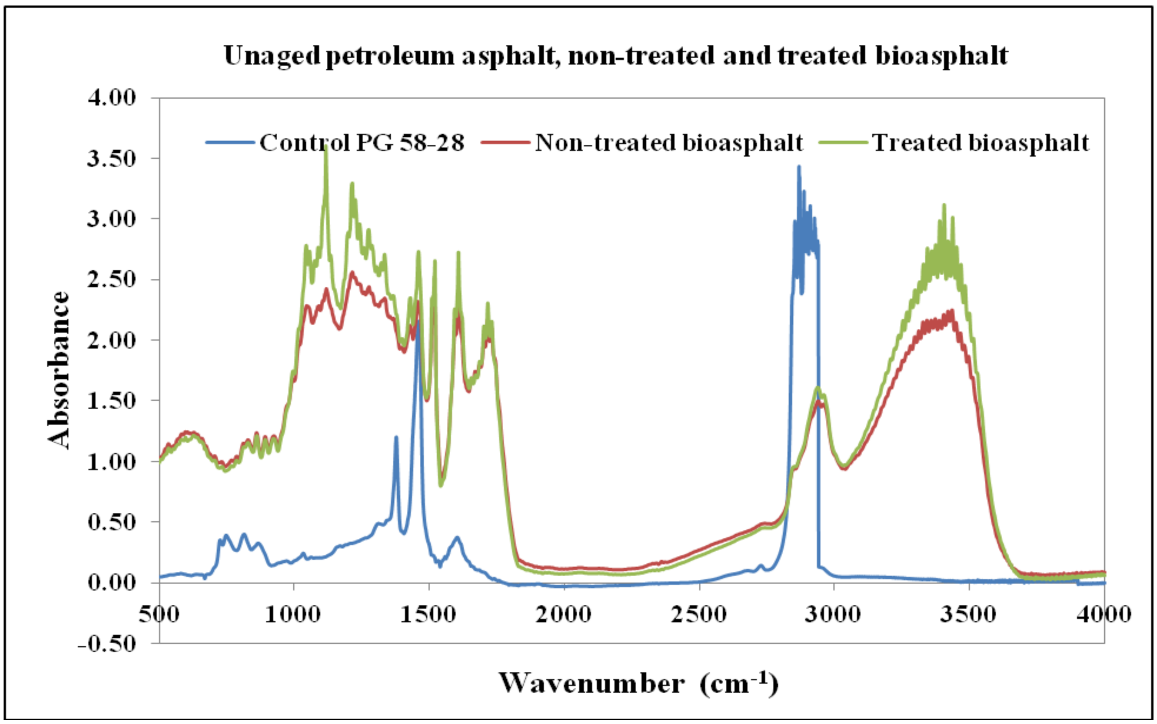


Figure 3-2: FTIR spectra for pure petroleum asphalt (PG 58-28), untreated and treated bioasphalt at their unaged condition

The prevalence of oxygen in the bioasphalt is distributed in different functional groups. The multiple oxygen occurring compounds and thus functional groups adds to make the ph of the bioasphalt about 2.5. It would be interesting to ascertain how the acidic pH level of this type of bioasphalt impacts on the petroleum-based PG 58-28 binder in terms of moisture susceptibility. The oxygen-related functional groups appear in the forms of the esters, ketones and carboxylic acids. And it is believed that their quantity and prominence could influence any oxidative hardening phenomenon occurring when the untreated and treated pure bioasphalt are used to modify the control PG 58-28.

3.2.4 Morphological changes in the bio-modified PG 58-28 binder

Similar to the pure or unmodified specimens, FTIR absorbance spectra for the control and 2%, 5% and 10% bio-modified PG 58-28 binder is provided in Figure 3-3 at their unaged conditions. From Figure 3-3, it is evident that the absorbance growth heights increased with increasing amounts of the untreated bioasphalt. It is believed that the modified PG 58-28 had higher bond strength between the molecules since the higher the rate of the untreated bioasphalt, the more the molecular functional groups can absorb the infra-red. From Figure 3-4, the control and 2% had a similar spectrum which was unexpected and could be attributed to excessive binder coating on the FTIR silicon slide surface. Typically, the 2% treated bio oil modified binder was anticipated to have higher absorption spectra curve than the control binder. Furthermore, the 10% treated bio oil modified absorption spectra is seen to be higher than that of the 5% modified.

Table 3-4: Functional groups identified for pure untreated and treated bioasphalt

Functional Group	Absorption wavenumber (cm^{-1})	Class of compound
C-H in plane bending	507 – 730	Aromatic compounds
C–O stretching, O-H bending	933 – 1390	Alcohols, ethers
C–H bending	1384 – 1482	Alkanes
–NO2 stretching	1482 – 1560	Nitrogenous compounds
N–H bending		Aromatic compounds
Aromatic C=C stretching		Aromatic compounds
C=O stretching	1650 – 1812	Ketones, carboxylic acids, aldehydes, esters, acyls

C-H stretching	2799 – 3040	Alkanes
O-H stretching	3045 – 3690	Polymeric O-H, water
N-H stretching	3045 – 3690	NH_2

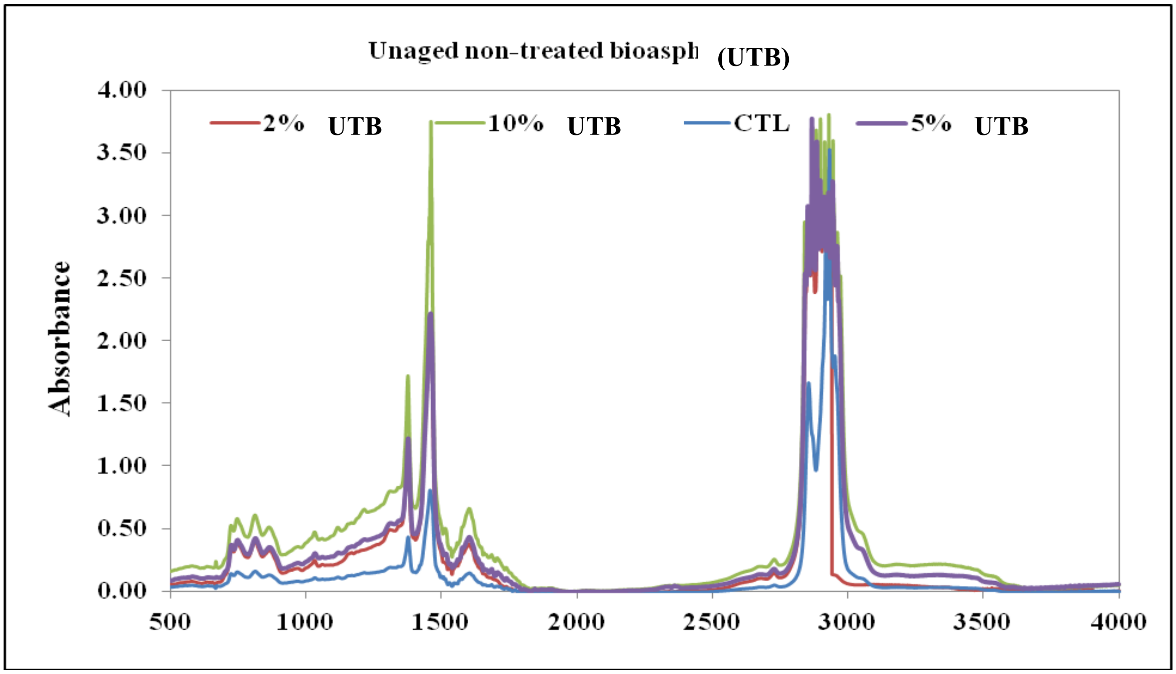


Figure 3-3: FTIR spectra for control and untreated bio oil modified PG 58-28 asphalt binders at unaged conditions

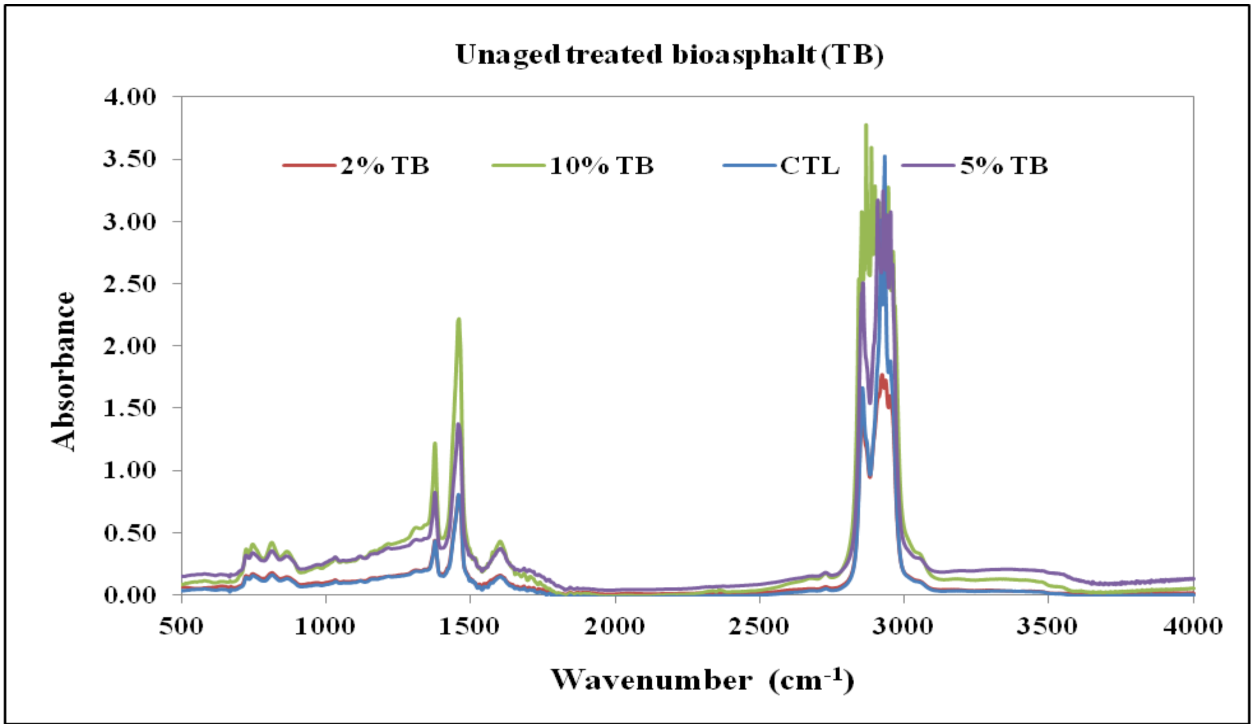


Figure 3-4: FTIR spectra for control and treated bio oil modified PG 58-28 asphalt binder at unaged condition

3.2.5 Carbonyl and sulphoxide aging behavior

The investigation of the carbonyl and sulphoxide bonding behavior within the PG 58-28 and bioasphalt modified binders are critical in understanding the morphological behavior of the samples at the chemical bonding level. This carbonyl and sulphoxide bonding, termed as the carbonyl and sulphoxide indices, respectively, was postulated to represent the degree of oxidative hardening or aging within organic compounds (Lamontagne 2001). From the FTIR spectra obtained for the control and bio oil modified specimens, the quantitative analysis of the carbonyl and sulphoxide indices is determined as shown in Equation 3-1 and 3-2.

$$I_{c=o} = \frac{Area\ of\ the\ carbonyl\ band\ around\ 1700 cm^{-1}}{Area\ of\ the\ spectral\ bands\ between\ 2000\ and\ 600\ cm^{-1}} \quad \textbf{(3-1)}$$

$$I_{s=o} = \frac{Area\ of\ the\ sulphoxide\ band\ around\ 1030 cm^{-1}}{Area\ of\ the\ spectral\ bands\ between\ 2000\ and\ 600\ cm^{-1}} \quad \textbf{(3-2)}$$

In order to investigate the rate of aging due to the carbonyl and sulphoxide bonds, these two indices are incorporated in the research. The aging indices are first conducted on the unaged materials and finally the RTFO and PAV aged specimens. This provides an understanding of the aging rates at the molecular bond level within the functional groups. Figure 3-5 and Figure 3-6 show the bar graphs of the results of the aging index analysis done on the control, untreated and treatedbioasphalt modified specimen. The results showed increasing carbonyl and sulphoxide aging indices with increasing rates of both the untreated and treated bioasphalt content. The functional groups in the untreated and treated bioasphalt are believed to interact with the functional groups of the PG 58-28 petroleum-based asphalt binder which results in formation of stronger bond network and thus an increase in the carbonyl and sulphoxide bonding indices. As asphalt binders typically undergo short and long-term aging, it was pertinent that the aging behavior of the RTFO and PAV aged specimens be investigated, respectively.

Figure 3-5: Bar chart of aging indices for unaged control and UTB modified asphalt binder

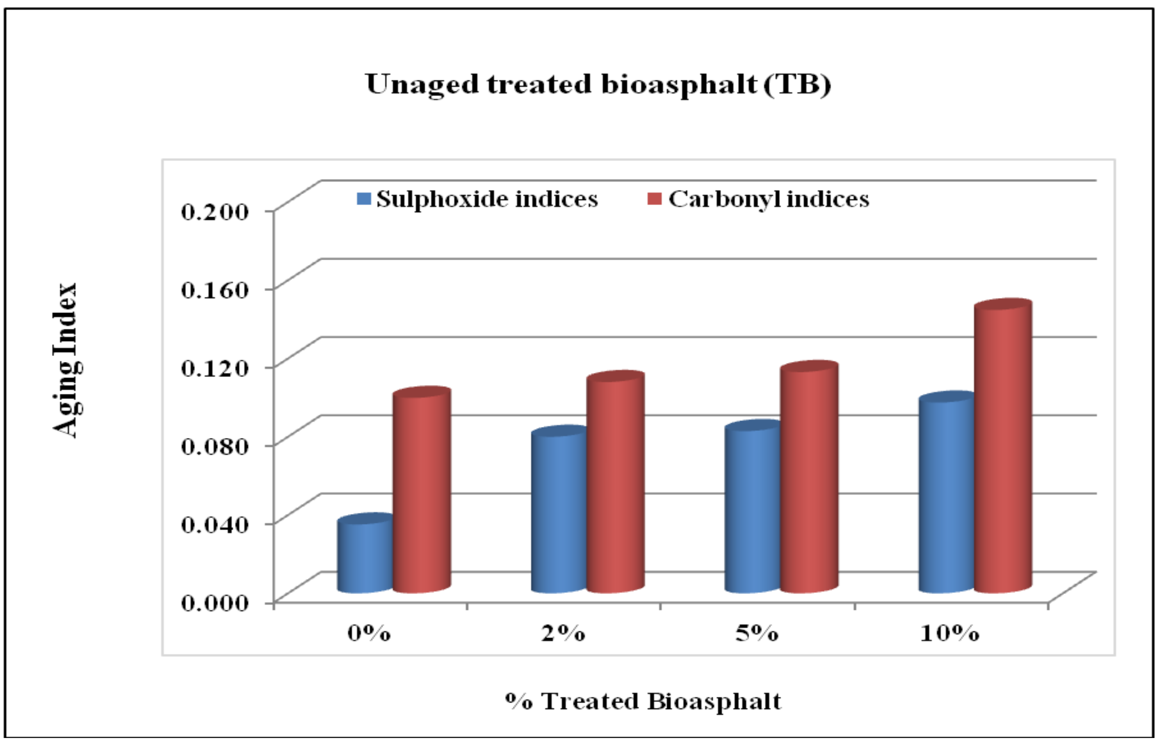


Figure 3-6: Bar chart of aging indices for unaged control and TB modified asphalt binders

From Figure 3-7 to Figure 3-10, the carbonyl and sulphoxide aging indices for both the untreated and treated bioasphalt samples after RTFO and PAV aging are provided in bar chart plots. Both the sulphoxide and carbonyl aging indices are observed to increase with increasing percent of the untreated and treated bioasphalt rate after RTFO and PAV aging. This can be attributed to the formation of stronger oxidation bonding chains initiated by the presence of the bioasphalt.

It is also observed that the aging indices for the untreated and treated bioasphalt samples are close to each other which means that after RTFO and PAV-aging, the effect of the moisture and volatiles present in the untreated bioasphalt have been reduced and the untreated bioasphalt molecular structure is similar to that of the treated specimen.

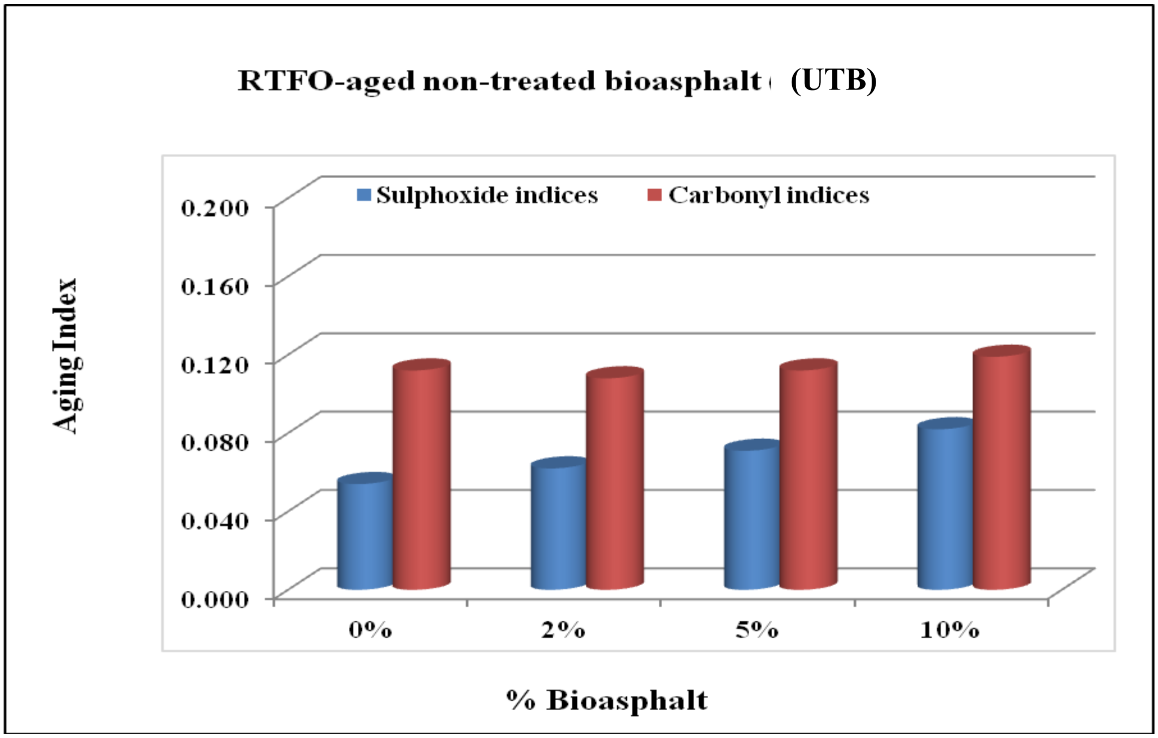


Figure 3-7: Bar chart of aging indices for RTFO-aged control and untreated bioasphalt

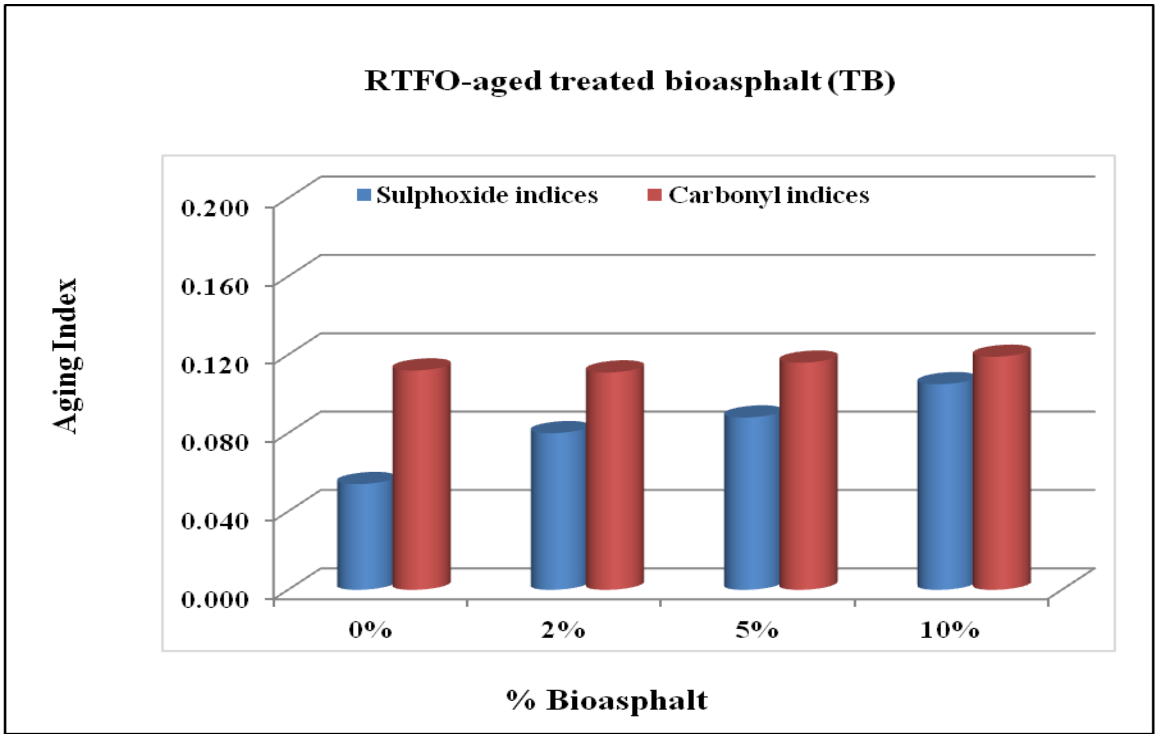


Figure 3-8: Bar chart of aging indices for RTFO-aged control and treated bioasphalt

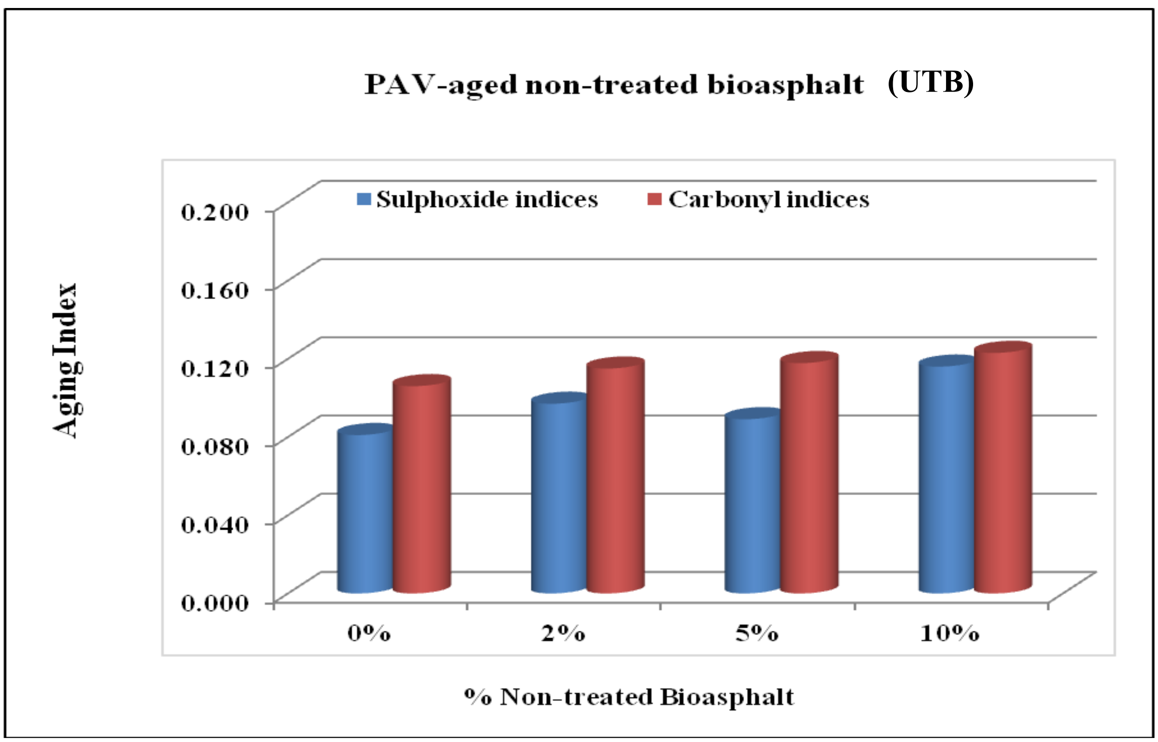


Figure 3-9: Bar chart of aging indices for PAV-aged control and untreated bioasphalt

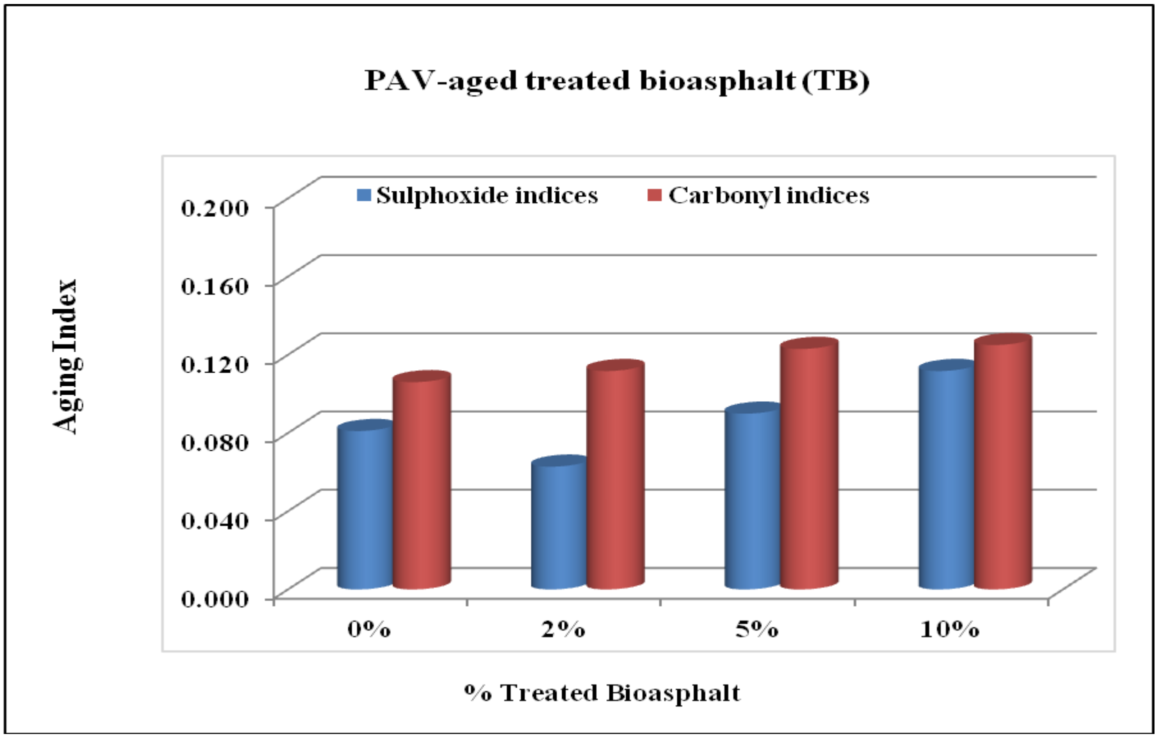


Figure 3-10: Bar chart of aging indices for PAV-aged control and treated bioasphalt

- ***AFT Results***

Due to limited bioasphalt materials, the AFT characterization was done on only the control and 2% bioasphalt modified PG 58-28 asphalt binder. This was considered satisfactory since the idea behind the AFT investigations was to ascertain what happens to the flocculation of asphaltene molecules in the petroleum-based PG 58-28 asphalt binder upon adding the bioasphalt sample.

The compatibility between the bioasphalt and the petroleum-based PG 58-28 asphalt binder was studied based on Equation 3-3 and the Wiehe compatibility model (Wiehe and Kennedy 2000).

$$\delta_{cr} = \Phi_0\delta_0 + \Phi_{10}\delta_{10} + \Phi_T\delta_T,\ \Sigma\Phi_i = 1 \qquad \textbf{(3-3)}$$

Where:

$\Sigma\Phi_i = 1$

δ_{cr}= the critical solubility constant

Φ_0 = volume fraction of bioasphalt-PG 58-28 blend

δ_0 = solubility constant of asphalt

Φ_{10} = volume fraction of iso-octane

δ_{10} = solubility constant of iso-octane (titrant), δ_{10} is 6.99 (cal/mL) $^{0.5}$ for iso-octane (titrane)

$\Phi_T\delta_T$= volume fraction of toluene, and solubility constant of toluene, $\delta_T$is 8.93 for toluene (solvent).

The measure of the solvency of the asphalt oil fractions (maltene) for the asphaltene fractions is given by equation (3-4).

$$S_{BN} = 100\frac{(\delta_{oil} - \delta_{10})}{(\delta_T - \delta_{10})} \quad \textbf{(3-4)}$$

Where:

δ_{oil}= solubility constant of the bioasphalt-PG 58-28 blend

δ_{10} = solubility constant of iso-octane (titrant); δ_{10} is 6.99 (cal/mL)$^{0.5}$ for iso-octane (titrane)

δ_T= solubility constant of toluene; $\delta_T$is 8.93 for toluene (solvent)

- ***Light transmittance-time curve analysis***

In Figure 3-11 and 3-12, the trace of light intensity versus time is given for the flocculation titration on the 0 and 2% bioasphalt modified PG 58-28 asphalt binder, respectively. The results are for three replicate tests. In the first part of the curve, the light transmission intensity increases because the asphaltenes remain in solution while the bioasphalt modified PG 58-28 asphalt binder matrix is being diluted gradually. At this stage, the concentration of the bioasphalt modified PG 58-28 asphalt binder matrix decreases with the addition of the titrant, iso-octane. The relevant equation, equation (3-5), to model this process has earlier been investigated:

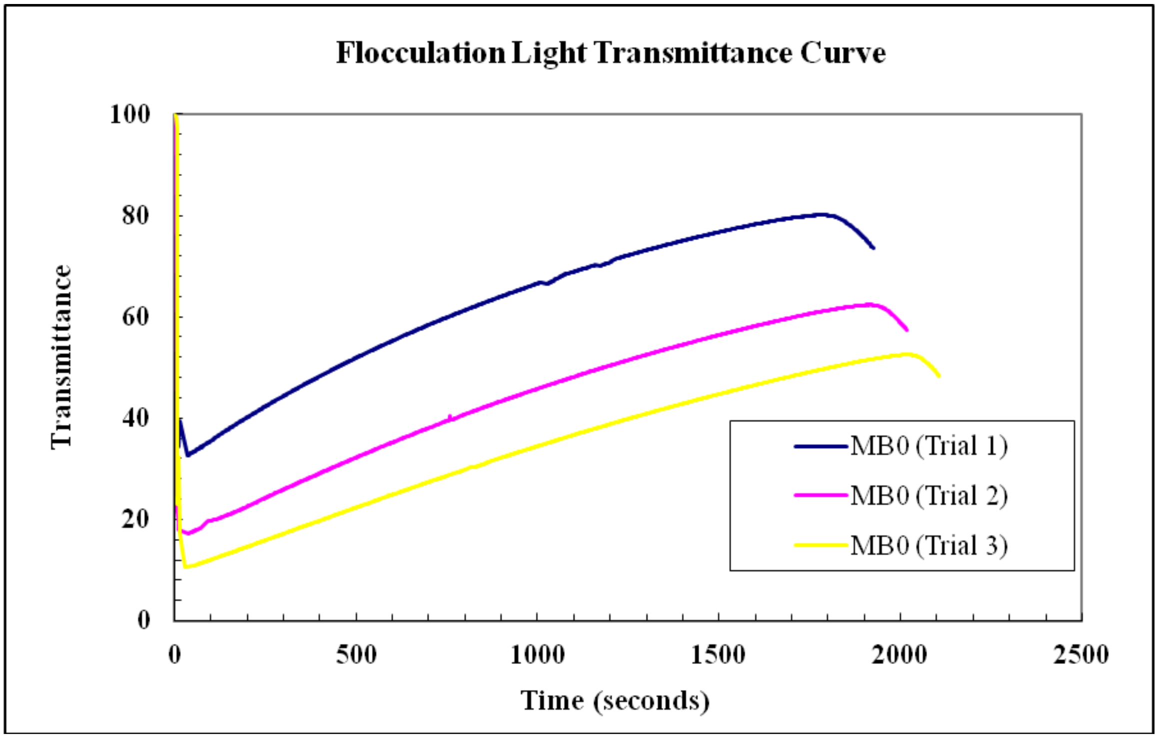


Figure 3-11: Titration time against light transmittance for control PG 58-28 binder (0% bioasphalt)

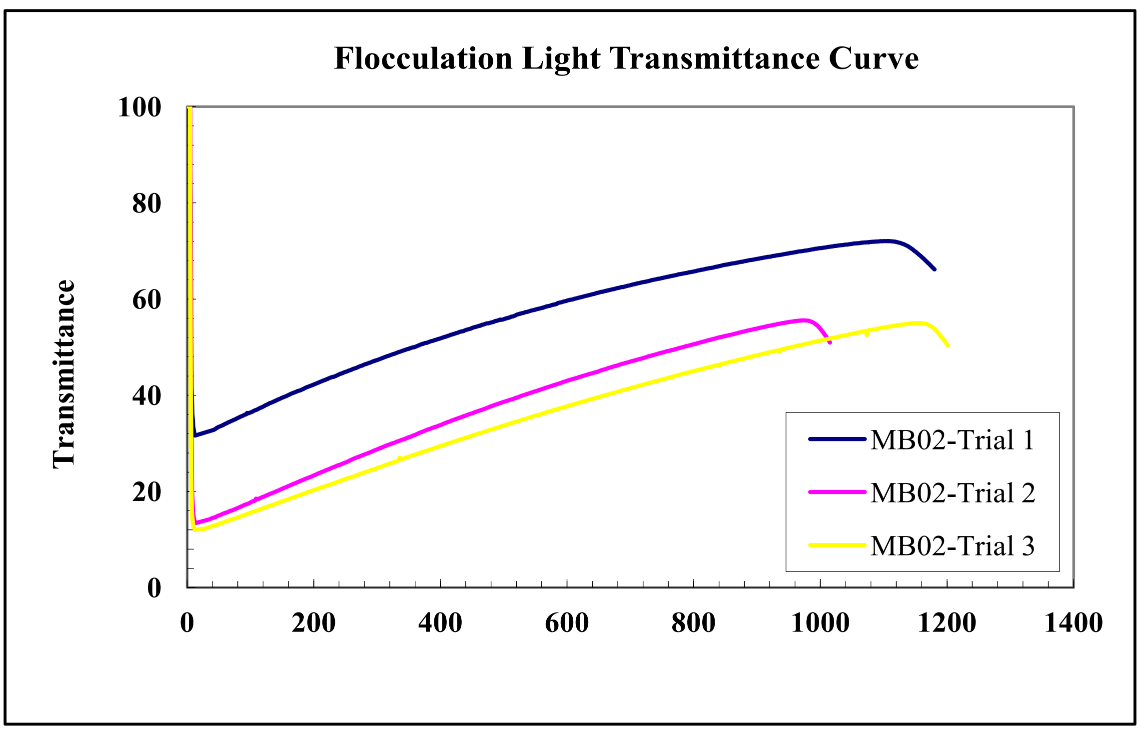


Figure 3-12: Titration time against light transmittance for control PG 58-28 binder (0% bioasphalt)

$$c_i = (V_0/(V_0 + V_t))\, c_0 \qquad \textbf{(3-5)}$$

Where:

c_0 = the initial oil concentration;

V_0 = the initial volume of sample;

Vt = volume of iso-cotane titrant

From Figure 3-11 and Figure 3-12, the transmittance all drop in value before beginning to rise. This initial drop is because at the start of the investigations, the PG 58-28 (0% bioasphalt) binder or 2% bio oil modified PG 58-28 binder alone is added to the toluene solvent. This leads to an increase in concentration of the mixtures and thus a decrease in light transmittance. Upon commencement of the flocculation titration process by addition of the titrant iso-octane, the PG 58-28/toluene or 2% bio oil modified PG 58-28/toluene mixtures begins to undergo dilution and thus increased light transmittance behavior. As the titration continues, a point is attained where the flocculation of the asphaltene molecules within the mixture starts. At the onset of this flocculation of these asphaltene molecules, scattering of the light rays will begin to occur and thus the transmittance intensities begin to decrease. It has been studied that at this maximum peak of light transmittance intensity, there is sufficient asphaltenes from the bioasphalt modified PG 58-28 asphalt binder matrix to scatter the light rays and this is the point where the dilution process is counteracted (Andersen 1999). The less steepness of the slopes in Figure 3-11 and Figure 3-12 suggests reasonably titration rate that is not too high and thus less severe local precipitation at equilibrium conditions.

- ***Flocculation ratio investigations***

In understanding and interpreting the results of the automated flocculation titrimetry, 2 approaches are used. Brief descriptions of the two approaches are shown herein. A key parameter of interest is the flocculation ratio (FR) of the bioasphalt-PG 58-28 asphalt binder matrix. This flocculation ratio is defined as the minimum amount of the toluene solvent necessary to keep the asphaltenes of the bioasphalt-PG 58-28 asphalt binder matrix in solution in the precipitant-toluene mixture. This definition has been put forward by Heithaus (Heithaus 1962). Therefore, the FR is expressed as the volume fraction of the solvent at the onset of the precipitation of the asphaltene content. Another interesting parameter used in the investigations is the inverse dilution ratio (I/X) or concentration of the mixture (C in g/mL), defined as the ratio of the volume of asphaltene precipitant to the volume of mass residue. The relevant equations used in evaluating the FR and the C parameters are:

$$FR = Vs / (Vs + Vt) \quad \textbf{(3-6)}$$

$$C = Wa / (Vs + Vt) \quad \textbf{(3-7)}$$

Where:

FR = flocculation ratios (FR)

Wa = weights of asphalt

Vs = Constant volume of toluene solvent

Vt = Volume of titrant (VT) required to initiate flocculation

The Heithaus parameters of interest from the investigations are: 1) C_{min}, defined as the quantity of the iso-octane titrant that would be just enough to cause asphaltene precipitation in the 0 and 2% bioasphalt PG 58-28 binder; 2) FR_{max}, defined as a measure of the solubility parameter, at which asphaltene flocculation occurs in the bioasphalt-PG 58-28 binder matrix as a whole. The peptizing power (P_o), peptizability of the asphaltenes (P_a) and the state of peptization (P) of the control PG 58-28 on one hand and the treated bioasphalt-PG 58-28 asphalt binder matrix can then be determined from Equation (3-8), (3-9) and (3-10).

$$P_o = FR_{max}(X_{min} + 1) \quad \textbf{(3-8)}$$

$$P_a = (1 - FR_{max}) \quad \textbf{(3-9)}$$

$$P = (X_{min} - 1) \quad \textbf{(3-10)}$$

Using FR_{max}, the insolubility number (I_N) can be calculated from equation (3-11).

$$I_N = 100 * FR_{max} \quad \textbf{(3-11)}$$

All the necessary Heithaus compatibility or solubility parameters are presented in Table 3-5. For stability of the asphaltenes in both the 0% and 2% treated bioasphalt samples, the insolubility number, I_N, which measures degree of insolubility of the asphaltene present must be less than the solubility blending number, S_{BN}, which measures the solvency of the oil for asphaltene.

Table 3-5: Compatibility parameters for 0 and 2% treated bioasphalt modified PG 58-28

Compatibility Parameters	0% (CTL)	2% (AFT M B0)
Flocculation ratio (FR)	0.321	0.361
C_{min}	0.526	5.319
Solubility number (S_{BN})	105.98	44.45
Heithaus (Fr_{max})	0.365	0.366
Peptizing power (P_o)	1.06	0.434
Peptizability of asphaltenes (P_a)	0.635	0.34
State of peptization (P)	2.9	1.188
Insolubility number (I_N)	36.53	36.56

From Table 3-5, the S_{BN} for both the 0% and 2% treated bioasphalt modified PG 58-28 asphalt binder are greater than their I_N; thus adding the bioasphalt to the conventional PG 58-28 asphalt creates a stable and compatible mixture. However, the S_{BN} of the 0% bioasphalt (control PG 58-28) was lower than the S_{BN} of the 2% treated bioasphalt modified PG 58-28 suggesting that modifying petroleum-based asphalt with treated bioasphalt can cause some of the asphaltene fractions to be unstable; but not sufficient enough to cause insolubility and thus initiate phase separation problems for the mixture.

In all cases, the P_o, P_a and P of the 2% treated bioasphalt modified PG 58-28 were found to be lower than those of the control (unmodified) PG 58-28. In terms of the peptizing power, P_o, it can be deduced that once the 2% treated bioasphalt was added to the control PG 58-28, the solvent power of the maltene fractions in the binder matrix was reduced at the final stage after the asphaltenes had began to flocculate. The overall compatibility of the asphaltenes in the maltenes of the PG 58-28, P value, is better than the 2% treated bioasphalt modified samples.

3.3 Conclusions

The characterization of the physio-chemical aging performance of pure wood waste bioasphalt and bio oil modified petroleum-based asphalt is done using the Fourier Transform Infra-red Spectroscopy (FTIR) technique. The degree of compatibility between the bioasphalt and a PG

58-28 asphalt binder are also investigated by employing the Automatic Flocculation Titration (AFT) process.

The conclusions drawn from the GC-MS and FTIR investigations are:

1) Levo, 2,6-dimethoxyphenol, 2 methoxy 4 vinylphenol, 2 methoxy-4-methylphenol, 2 methoxyphenol, 2 methyl 1-2 cyclopentandione, 4-allyl-2, 6 dimetoxyphenol, 3 methyl-1-2 cyclopentandione, 3, 5, dimethoxy-4-hydrobenzaldehyde, furfural, phenol, o-cresol, m-cresol, p-cresol, eugenol and isogenol are the individual chemical compounds present in this waste-wood bioasphalt.
2) The classes of compounds are aromatic compounds, nitrogenous compounds, alcohols, ethers, ketones, carboxylic acids, aldehydes, esters, acyls alkanes, polymeric O-H, NH_2 and water.
3) The FTIR absorbance peak heights increased with increased amounts of 2, 5 and 10% of untreated and treated bioasphalt. Thus, the presence of the bioasphalt increased the bond strengths of the traditional PG 58-28 asphalt binder. Carbonyl and sulphoxide oxidative hardening indices increased with increasing bioasphalt rate after RTFO and PAV aging.

Before bioasphalt from the combined waste-wood blend was used as a modifier in petroleum-based asphalt, the degree of molecular compatibility between the two compounds was investigated with the aid of the automated flocculation titrimetry (AFT) technique. The test data was used to estimate the colloidal stability of the bioasphalt –petroleum asphalt cross blends. Based on the AFT investigations, the following conclusions can be drawn:

1) Treated bioasphalt, containing limited quantities of water, can be successfully used as a modifier in petroleum-based asphalt with appreciable or desirable stability of the asphaltene fractions in the maltene medium of the petroleum-based asphalt.
2) Upon blending the treated bioasphalt into the petroleum-based asphalt, the degree to which the asphaltenes are freed into the maltene solvent fractions of the petroleum based

asphalt is reduced. This suggests that the treated bioasphalt holds back the ability of the higher molecular fractions (asphaltenes) to go into solution.

3) With the addition of higher rates of treated bioasphalts in petroleum-based asphalts, conglomeration or assemblage of the asphaltenes will be reached with possible undesirable stiffening effects or loss of some elastic characteristics of the asphalt binder.

CHAPTER 4: LABORATORY EVALUATION OF BIO OIL AS MODIFIER ON RHEOLOGICAL PROPERTIES OF ASPHALT BINDERS

4.1 Introduction

Asphalt binder is one of the three main components (binder, aggregate and air voids) of asphalt mixtures and the binder properties have important relationship with the short-term and long-term performances of asphalt mixtures. In addition, the rheological properties of virgin asphalt binders can also determine the mixing and compaction temperature of asphalt mixtures during the construction period. Rutting, thermal and fatigue cracking are the most concerned distresses that truncate or impede the pavement service ability and service life from functional and structural perspectives. The mixing and compaction temperatures have relation with the energy needed to heat the asphalt mixture materials and the emissions to the environment. A lower mixing and compaction temperature is encouraged nowadays for the energy saving and the environmental friendly. Rutting is described as the progressive permanent deformation in the pavement caused by the displacement of the asphalt mixture particles under wheel load especially at high temperatures. Thermal cracking, also called as low temperature cracking, occurs when the tensile stress or strain exceed the stress or strain capacity of asphalt pavement at low temperatures. Normally, thermal cracking occurs from the surface of asphalt pavement. Fatigue cracking is caused by the repeated tensile strength. Although the tensile stress or strain is lower the capacity of the asphalt pavement, the repeated stress would also cause a cracking finally. Since the asphalt binder properties has close relation with the performance of asphalt mixtures, some testing methods for asphalt binder properties have been well developed to indicate the potential performance of asphalt mixtures.

4.2 RV Test Results

4.2.1 RV test for virgin asphalt binders

Figure 4-1 to Figure 4-3 display the rotational viscosities of control binder PG 58-28 and UTB, TB and PMB modified asphalt binders at the temperatures of 90°C, 110°C, 130°C, 150°C and 165°C before RTFO aging. Based on the test results, it is observed that the rotational viscosities of 5% and 10% UTB modified asphalt binders were 13.3% and 7.7% lower than the control asphalt binder in average, respectively; the rotational viscosities of 5% and 10% TB modified asphalt binders were 12.1% and 7.6% lower than the control asphalt binder in average, respectively; the rotational viscosities of 5% and 10% PMB modified asphalt binders were 8.4% and 12.4% lower than the control asphalt binder in average, respectively.

The test results mean that the addition of bio oil as a modifier can reduce the rotational viscosity compared to the control asphalt binder PG 58-28. The reduction of the rotational viscosity showed a consistence with the increase of the PMB percentage in the asphalt binder However, the reduction of the rotational viscosity was not consistent with the increase of the bio oil percent for UTB and TB modified asphalt binder since 5% bio oil modified asphalt binders showed the highest viscosities compared to the control binder and 10% bio oil modified asphalt binders.

Superpave™ binder test specification for PG 58-28 requires the rotational viscosity of asphalt binder at 135°C be less than 3Pa-s (3000cP). Based on the test result, an interpolation was made to estimate the rotational viscosities at 135°C. Because the rotational viscosities of control binder at 135°C were 300cP, and that the viscosities of bio oil modified asphalt binders were lower than the control binder, all of the asphalt binders investigated can meet the Superpave™ requirement.

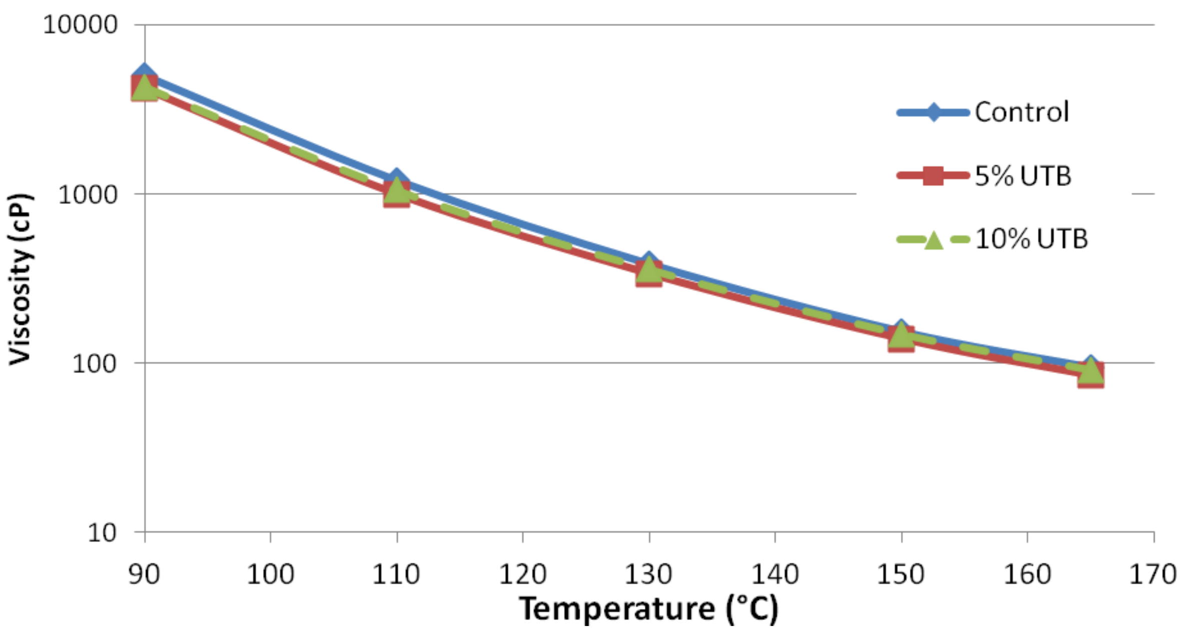


Figure 4-1: RV test results for control binder, 5%, 10% and 100% UTB modified asphalt binders before RTFO aging

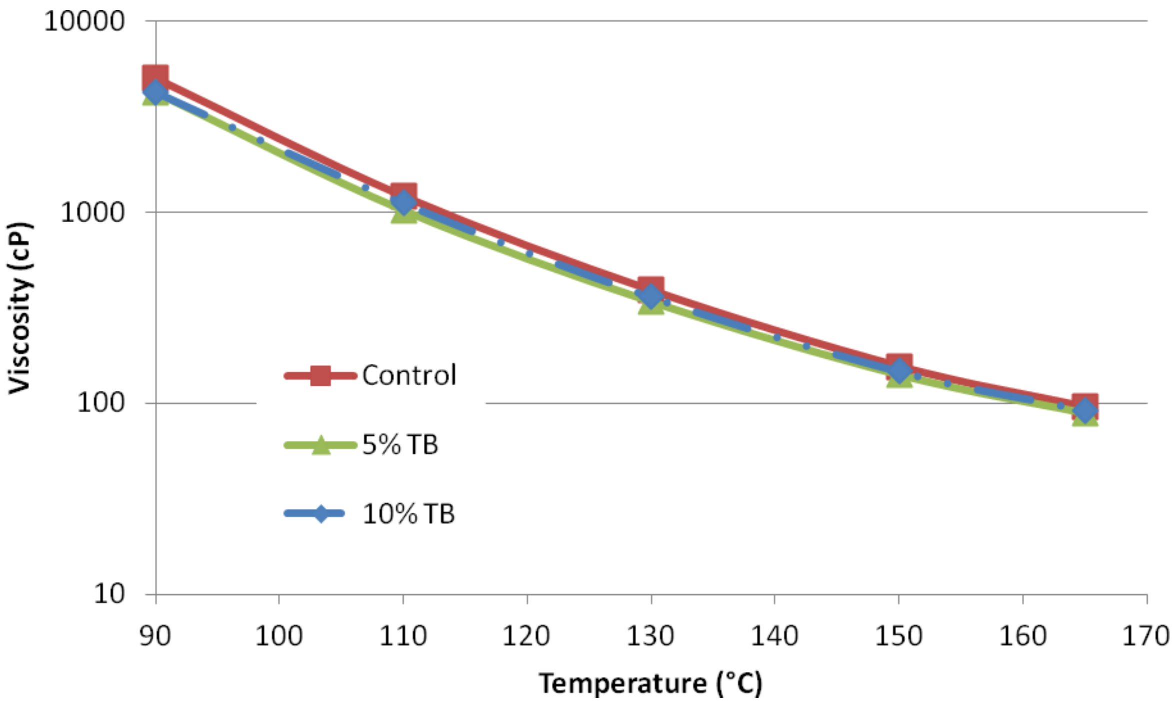


Figure 4-2: RV test results for control binder, 5%, 10% and 100% TB modified asphalt binders before RTFO aging

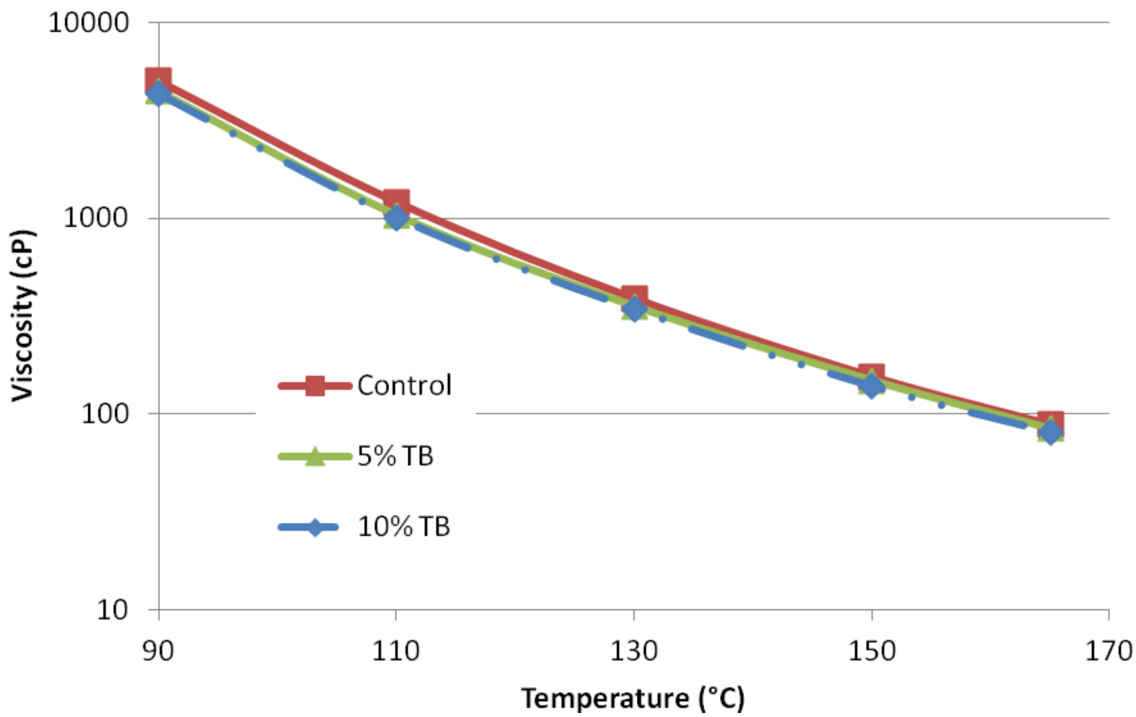


Figure 4-3: RV test results for control binder, 5%, 10% and 100% PMB modified asphalt binders before RTFO aging

4.2.2 RV Test for RTFO Aged Binders

The RV test for RTFO aged asphalt binders were also conducted at 90°C, 110°C, 130°C, 150°C and 165°C. Figure 4-4 to Figure 4-6 show the RV test results of control asphalt binder and three types of bio oil modified asphalt binders after RTFO aging. It is observed from Figure 4-4 that the rotational viscosities of 5% and 10% UTB modified asphalt binders were averagely 1.2% and 8.5% higher than that of the control binder respectively in the temperature range of 90°C to 165°C. Figure 4-5 shows that the rotational viscosities of 5% and 10% TB modified asphalt binders were averagely 2.9% and 14.9% higher than that of the control binder respectively in the tested temperature range. It is observed from Figure 4-6 that the rotational viscosities of 5% and 10% PMB modified asphalt binders were averagely -3.6% and -4.7% higher than that of the control binder respectively in the tested temperature range.

The test results showed that the bio oil modified asphalt binders obtained higher rotational viscosities than the control binder except the PMB modified asphalt binders, whose rotational viscosities were still slight lower than that of the control binder. This means that the bio oil modified asphalt binders were more susceptible to aging compared to the control binder.

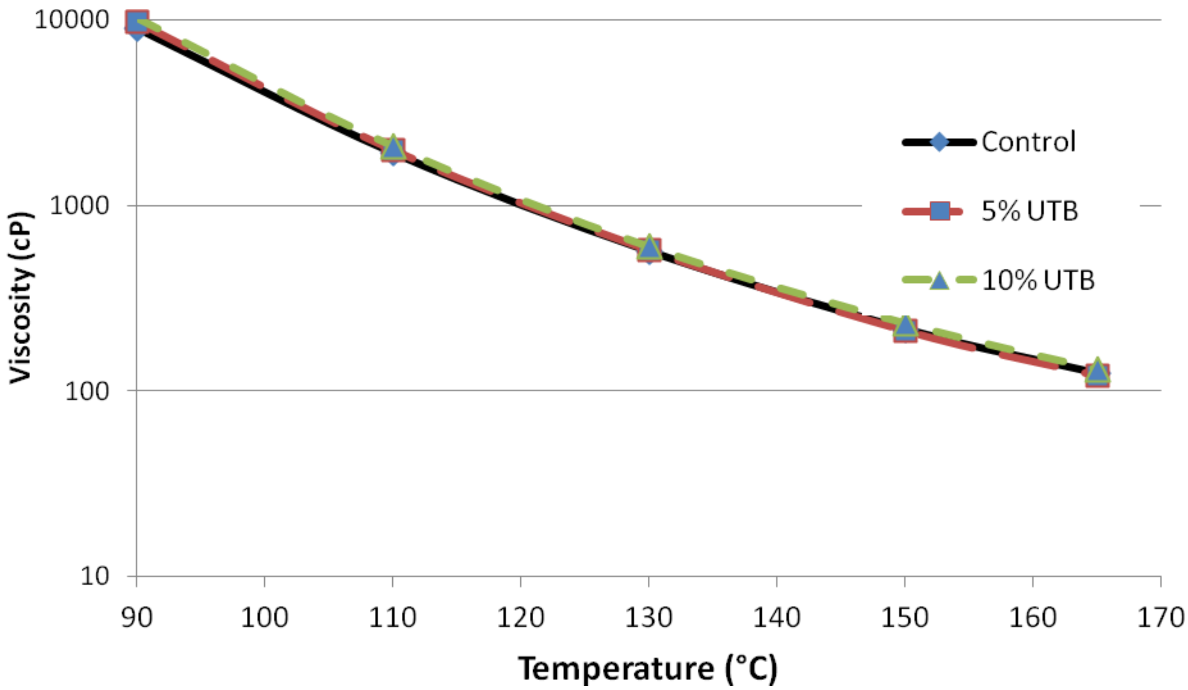


Figure 4-4: RV test results of control binder, 5%, and 10% UTB modified binders, after RTFO aging

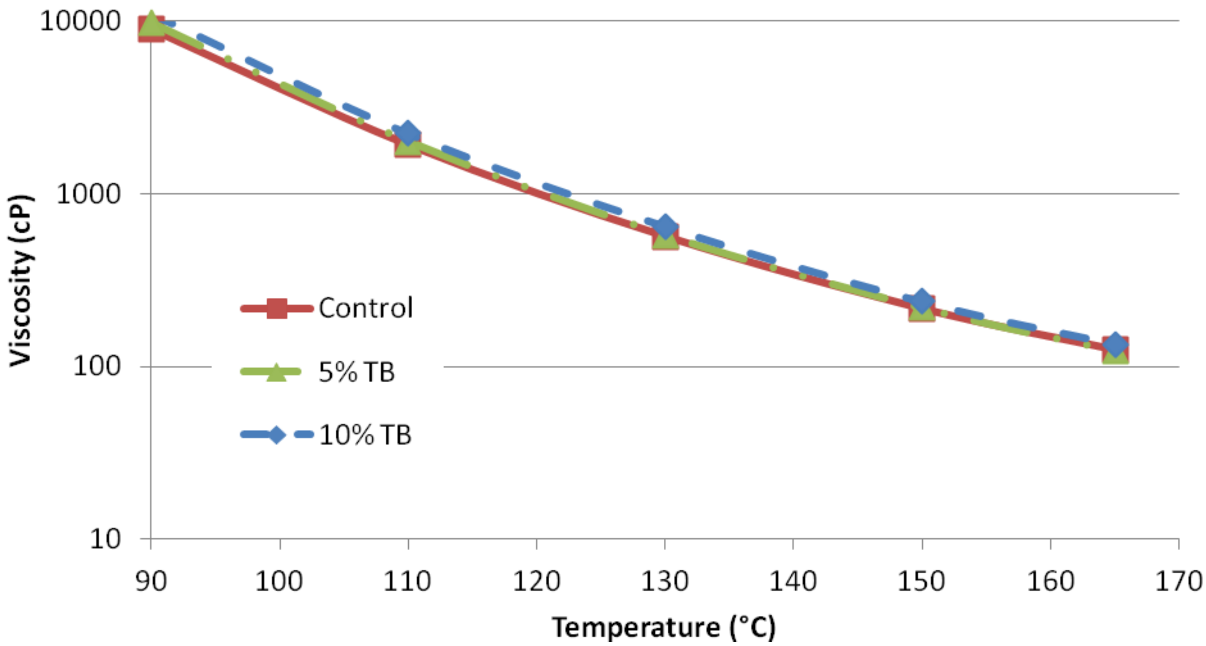


Figure 4-5: RV test results of control binder, 5%, and 10% UTB modified binders, after RTFO aging

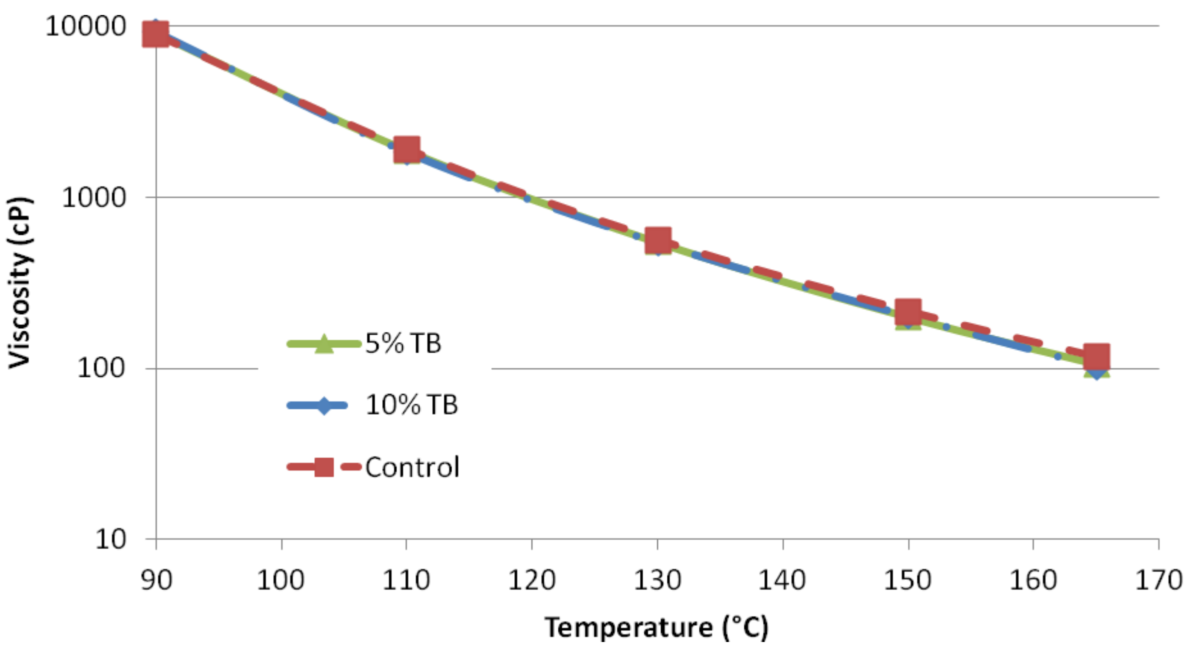


Figure 4-6: RV test results of control binder, 5%, and 10% UTB modified binders, after RTFO aging

4.2.3 Aging Index in High Temperature Ranges

The aging index of asphalt binders from RV test is determined as the ratio of the rotational viscosity values after and before the RTFO test, as shown in Equation 4-1.

Aging Index=Viscosity after RTFO/Viscosity before RTFO (4-1)

Figure 4-7 shows the aging indexes of control binder and bio oil modified asphalt binders in the temperature range of 90°C to 165°C. It is observed that with the increase of bio oil percentage in the asphalt binder, the aging index also increased. Compared to the control binder, the aging indexes of 5% and 10% UTB modified binders were 17.64% and 18.82% higher than that of the control binder respectively; the aging indexes of 5% and 10% TB modified binders are 18.15% and 26.13% higher than that of the control binder respectively; and the aging indexes of 5% and 10% PMB modified binders are 6.62% and 9.97% higher than that of the control binder respectively.

The aging index comparison among different types of bio-modified binders shows that the TB modified asphalt binder showed the highest aging index, followed by UTB and PMB. Because TB is a product after a process of reducing the water content of the UTB, it is thought that the volatilization of water during the aging process can reduce the aging effect bio oil. As a result, the aging index of UTB modified asphalt binder is lower than that of the TB modified binder. The lower aging index of PMB modified asphalt binder may due to the effect of polymer in the binder.

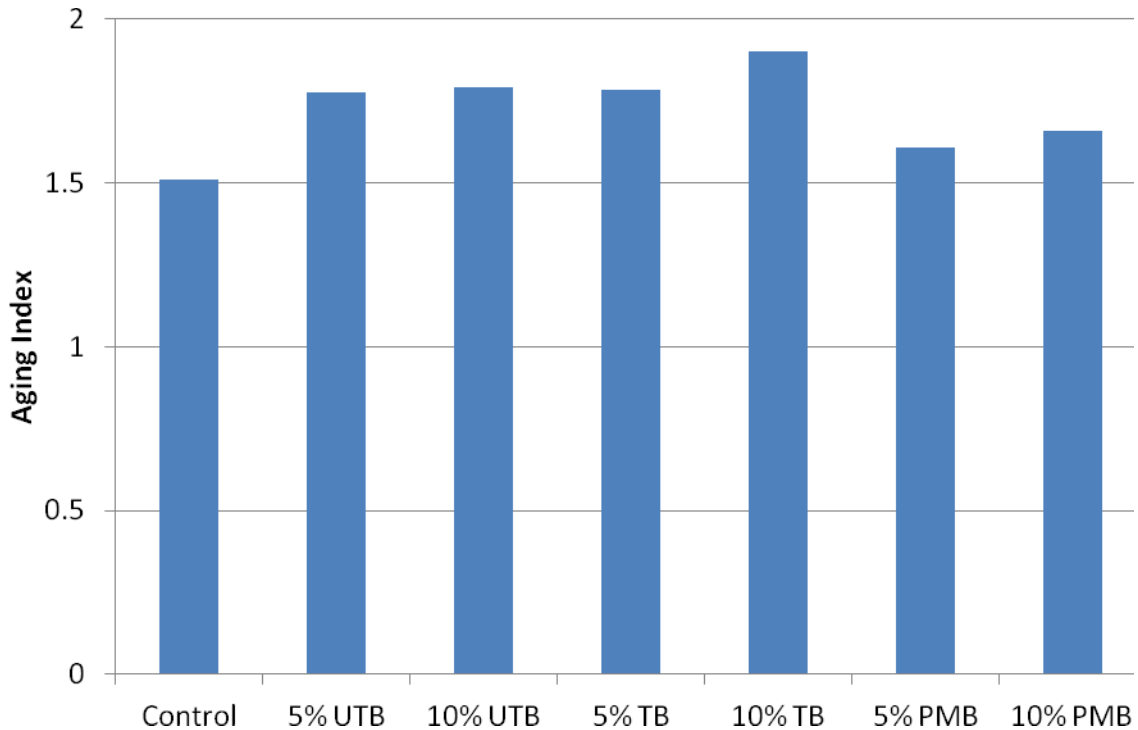


Figure 4-7: Average aging index of control binder and bio oil modified asphalt binders at temperature 90°C, 110°C, 130°C, 150°C and 165°C from RV test

4.3 DSR Test Results

4.3.1 DSR test for virgin binders

As mentioned before, the DSR test for virgin binders were conducted at temperatures of 40°C, 46°C, 52°C, 58°C, 64°C and 70°C. The test frequencies selected were 0.01Hz, 0.1Hz, 1Hz, 5Hz, 10Hz and 25Hz. Figure 4-8 to Figure 4-10 illustrate the complex shear modulus (|G*|) results of control binder and bio oil modified asphalt binders.

Figure 4-8 shows that the 5% and 10% UTB modified asphalt binders showed lower |G*| than the control binder in high reduced frequency area (>1Hz, low temperature and high frequency) but showed higher |G*| in low reduced frequency area (<0.01Hz, high temperature and low frequency). Since the rutting normally occurs at high temperature and low traffic speed conditions which accords with the low reduced frequency area in the DSR test, the test results indicates that the 5% and 10% PMB modified asphalt binders can acquire better high temperature performances than the control binder PG 58-28.

Figure 4-9 shows the |G*| of control binder, 5% and 10% TB modified asphalt binders. The test results were similar as that of the UTB modified binders. It is found that the 5% and

10% UTB modified asphalt binders showed lower |G*| than the control binder in high reduced frequency area (>1Hz, low temperature and high frequency) but showed much higher |G*| in low reduced frequency area (<0.01Hz, high temperature and low frequency). Based on the test result, it is also expected that the 5% and 10% TB modified asphalt binders can perform better rutting resistance than the control asphalt binder.

Figure 4-10 shows the |G*| results for control asphalt binder, 5% and 10% PMB modified asphalt binders. Unlike what happened in the UTB and TB modified binder tests, the PMB modified asphalt binders showed slightly higher |G*| than the control binder in both high reduced frequency area and low reduced frequency area. This may result from the enforcement of polymer to the asphalt binders. Thus, the test results also indicated that the PMB modified asphalt binders are expected to gain higher rutting performance than the control binder.

To make the comparison for the three types of bio oil modified binders, it is found that the PMB modified asphalt binder has higher complex shear modulus than the UTB and TB modified asphalt binder and is expected to gain higher rutting performance than the other two types of bio oil modified asphalt binders.

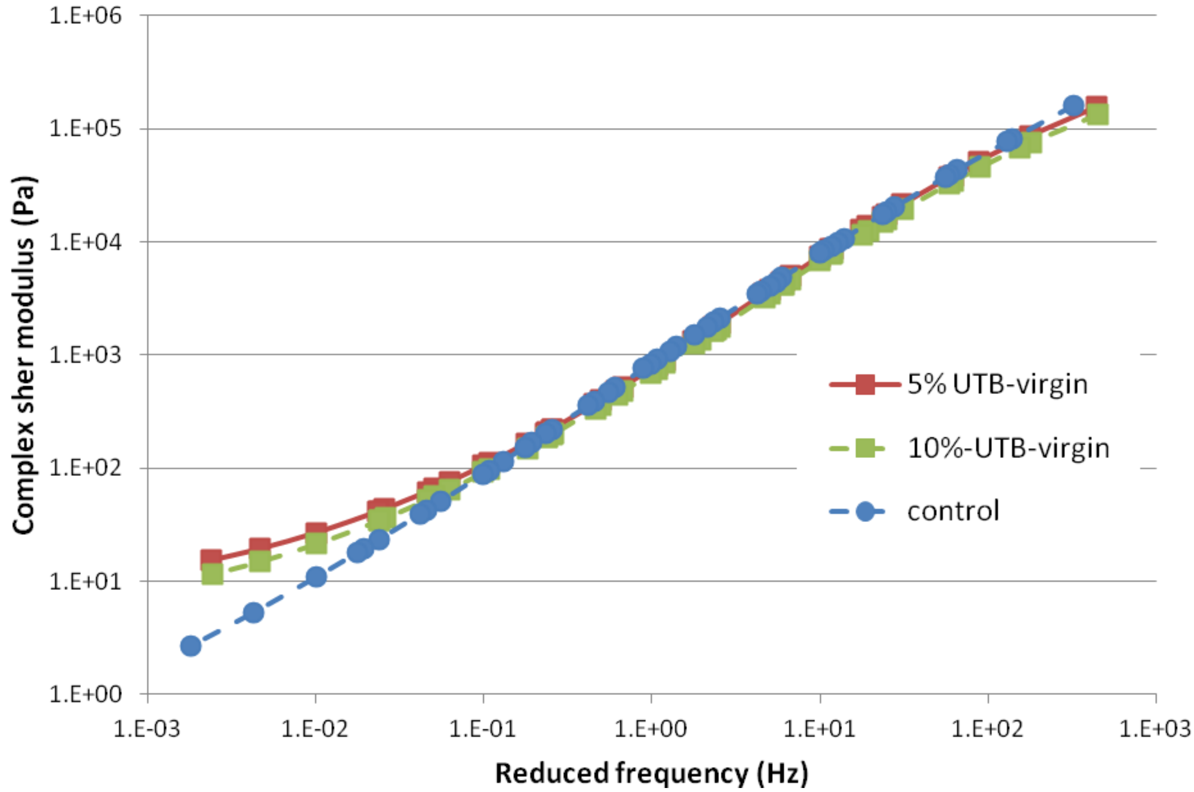


Figure 4-8: G* master curve plot for control binder, 5% and 10% UTB modified asphalt binders before RTFO aging

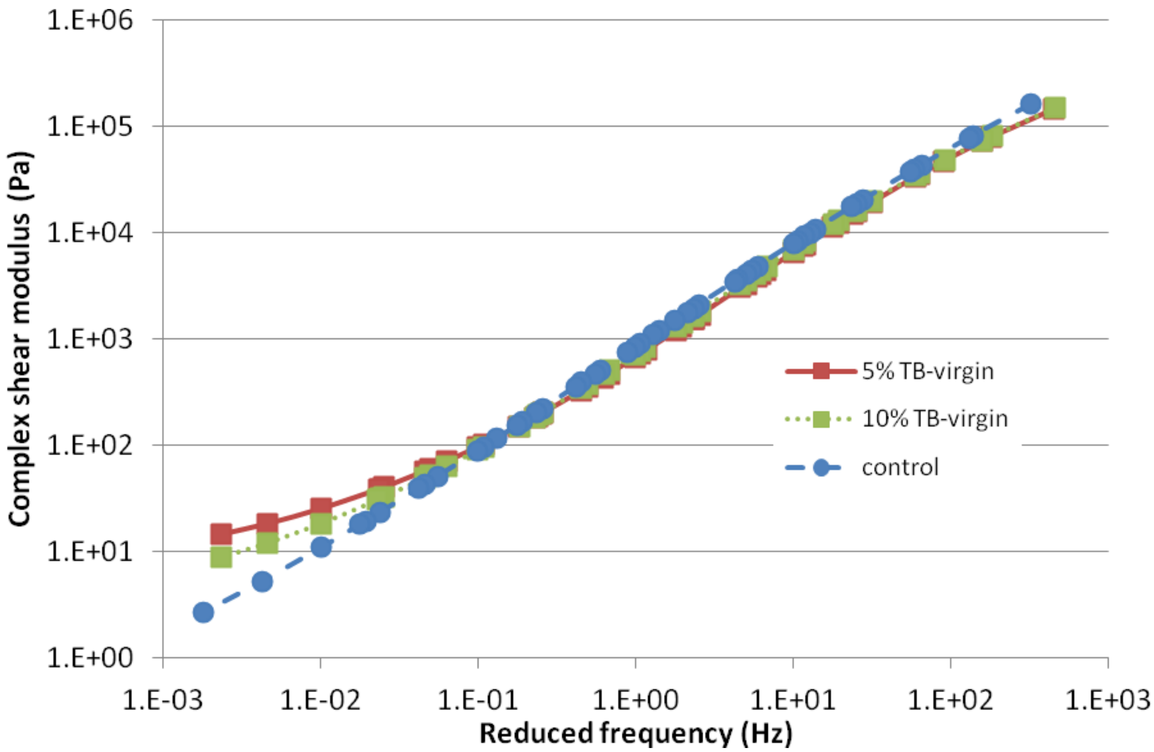


Figure 4-9: G* master curve for control binder, 5% and 10% TB modified asphalt binders before RTFO aging

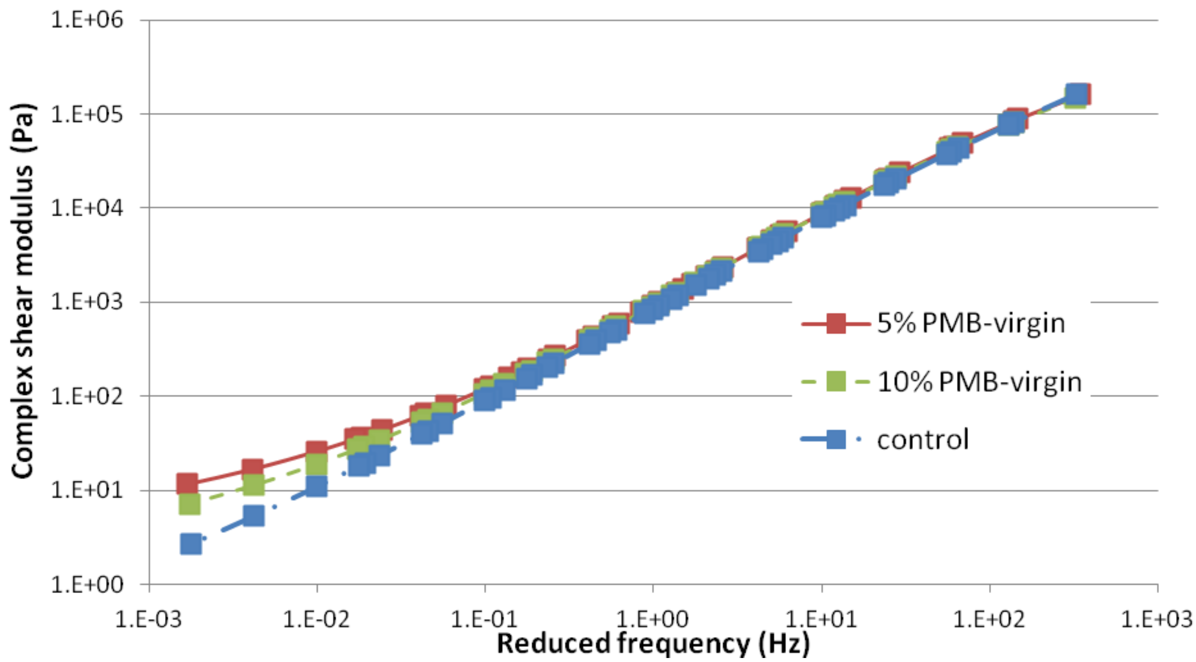


Figure 4-10: G* master curve for control binder, 5% and 10% PMB modified asphalt binders before RTFO aging

4.3.2 DSR Test for RTFO Aged Binders

The DSR test for RTFO aged asphalt binders in this study were also conducted at 40°C, 46°C, 52°C, 58°C, 64°C and 70°C. The test frequencies selected were 0.01Hz, 0.1Hz, 1Hz, 5Hz, 10Hz and 25Hz. Figure 4-11 to Figure 4-13 plot the |G*| master curve for control binder and bio oil modified asphalt binders in the DSR test after RTFO aging.

It is observed that the |G*| of bio oil modified asphalt binders were higher than that of the control binder after RTFO aging. The |G*| of 5% and 10% UTB modified asphalt binders were 41.7% and 49.5% higher than that of the control binder in average, respectively; the |G*| of 5% and 10% TB modified asphalt binders were 41.2% and 71.3% higher than that of the control binder in average, respectively; the |G*| of 5% and 10% TB modified asphalt binders were 59.7% and 65.6% higher than that of the control binder in average, respectively. This result was mainly due to the high aging effect of bio oil added in the control asphalt binder. Superpave^{TM} binder test method specifies both the G*/sinδ before and after RTFO aging as an index to characterize the rutting performance. However, since rutting normally occurs after the pavement is placed, when the asphalt binder has experienced the short-term aging, it is more reasonable to characterize the rutting performance by only the G*/sinδ after RTFO aging. Based on this, it is anticipated that the bio oil modified asphalt binders can obtain higher rutting performance than the control binder for the much higher |G*| after RTFO aging.

To compare the rutting performances among the three types of bio oil modified asphalt binders, the TB and PMB modified asphalt binders showed higher |G*| than the UTB modified asphalt binder. There are mainly two reasons for this: 1) the TB modified asphalt binder aged faster than the UTB modified asphalt binder; 2) polymer in the PMB modified asphalt binder enhanced the modulus of the asphalt binder.

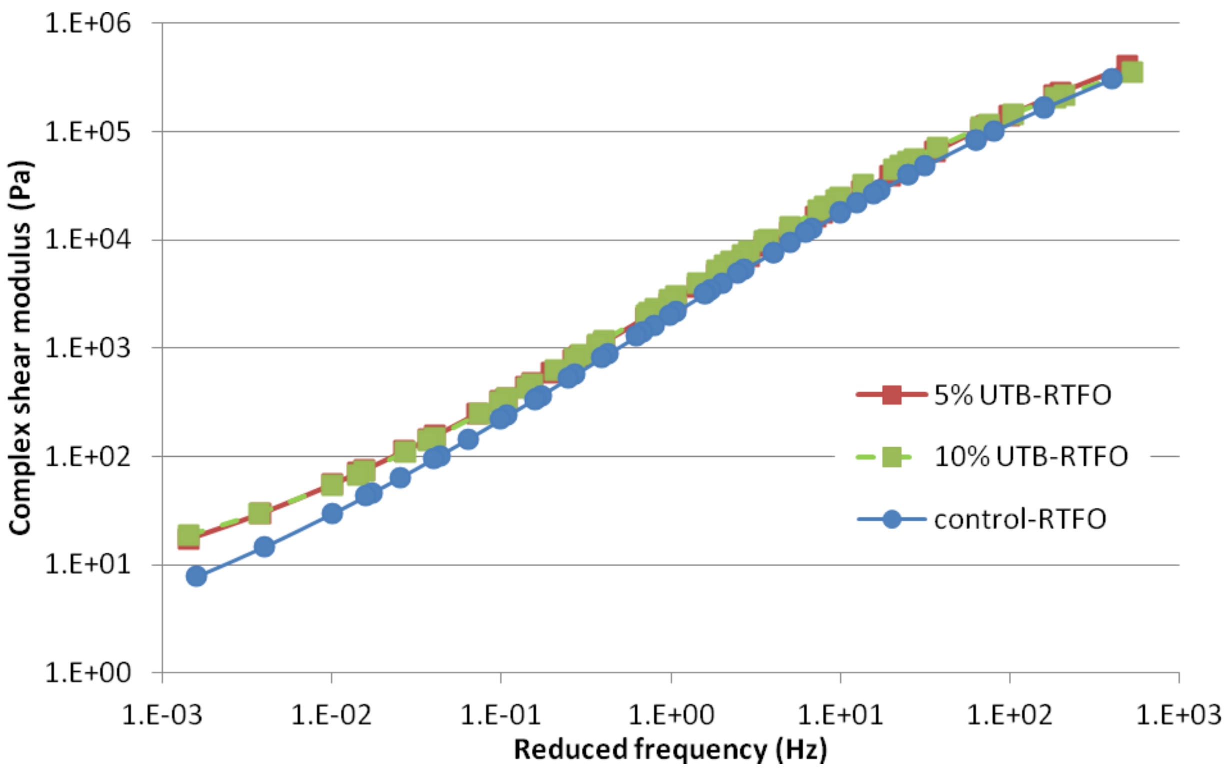


Figure 4-11: G* master curve plot for control binder, 5% and 10% UTB modified asphalt binders after RTFO aging

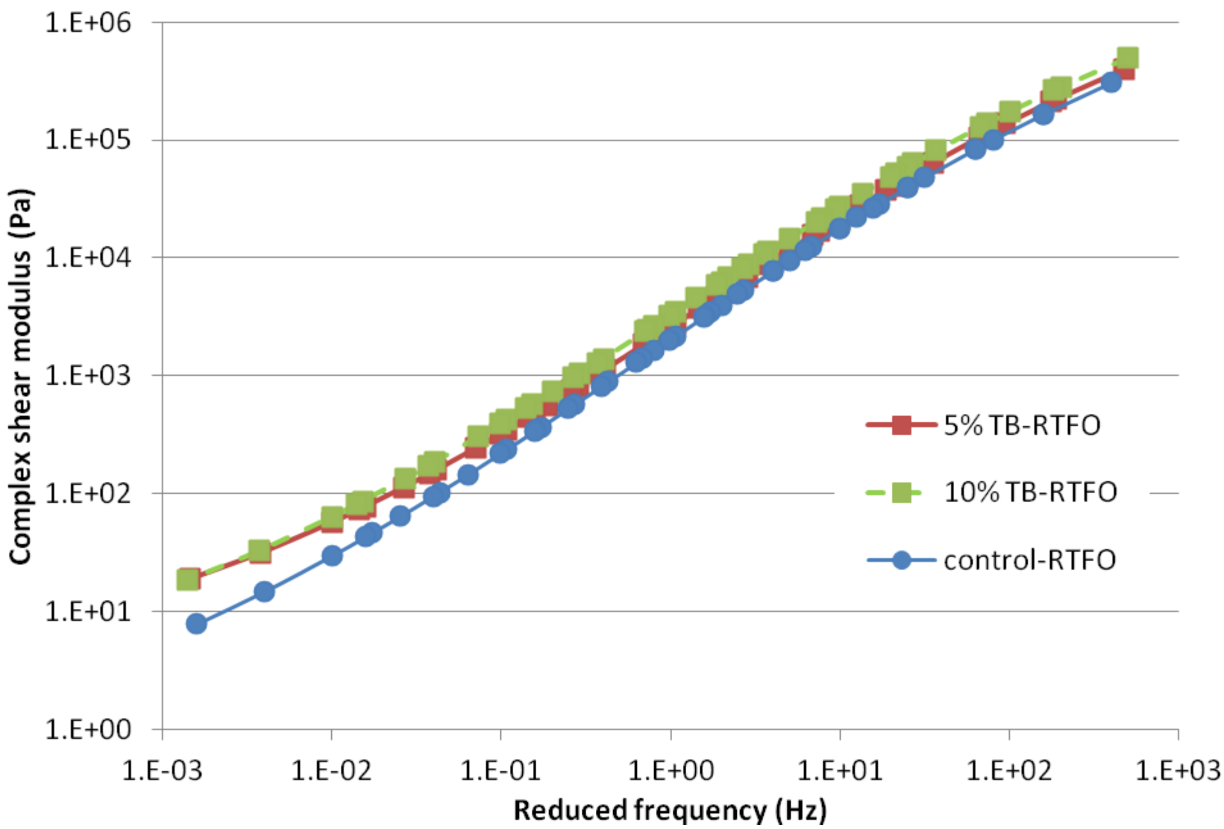


Figure 4-12: G* master curve plot for control binder, 5% and 10% TB modified asphalt binders after RTFO aging

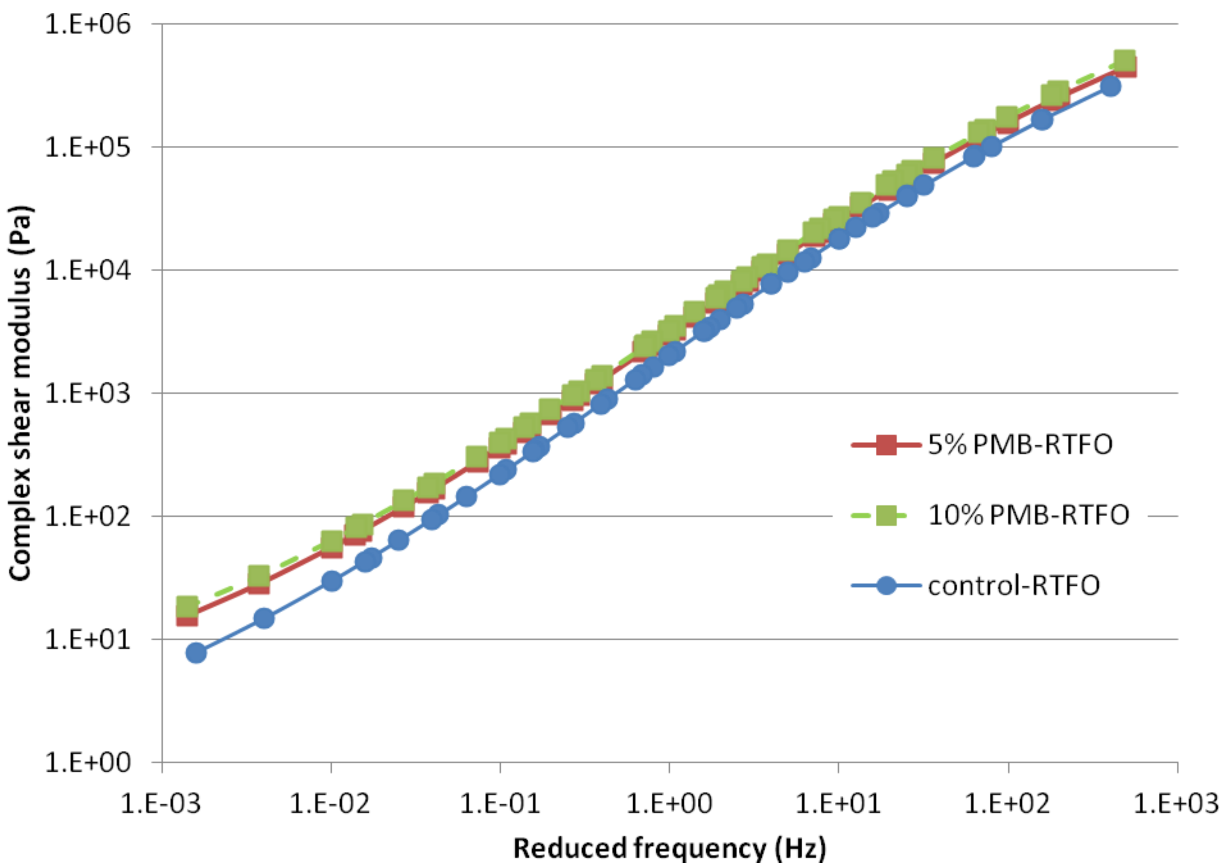


Figure 4-13: G* master curve plot for control binder, 5% and 10% PMB modified asphalt binders after RTFO aging

4.3.3 Aging Index in Low Temperature ranges

Aging index in low temperature ranges can be defined as the ratio between the G* after RTFO aging and that of virgin binders. It can demonstrate the effect of RTFO aging on the rheological properties of asphalt binders in low temperature ranges. The equation is expressed as follows:

$$\text{(Aging Index)}_{LT}=G^*\text{ after RTFO}/G^*\text{ before RTFO} \quad (4\text{-}2)$$

Figure 4-14 shows the aging indexes of control binder and bio oil modified asphalt binders in temperature range of 40°C to 70°C after RTFO aging. It is observed that with the increase of bio oil percentage in the asphalt binder, the aging index also increased. The aging index of the 5% and 10% UTB modified asphalt binders were 16.82% and 38.20% higher than that of the control binder respectively; the aging indexes of the 5% and 10% TB modified asphalt binders were 28.47% and 58.68% higher than that of the control binder respectively; the aging indexes of the 5% and 10% PMB modified asphalt binders were 24.02% and 41.19% higher than that of the control binder. The fast aging of bio oil in this study is consistent with some previous studies using bio oil from fast pyrolysis (Raouf and Williams 2009; Mills-Beale et al. 2012; Onochie et al. 2013).

To compare the aging indexes of three types of bio oil modified asphalt binders, the TB modified asphalt binder showed the highest aging indexes, followed by the PMB modified asphalt binder and UTB modified asphalt binder. The reason may be that: 1) the water contained in the UTB help reduce the aging of the asphalt binder; 2) the polymer in the PMB increased the initial modulus before RTFO aging and reduced the increase percent of the modulus after the aging.

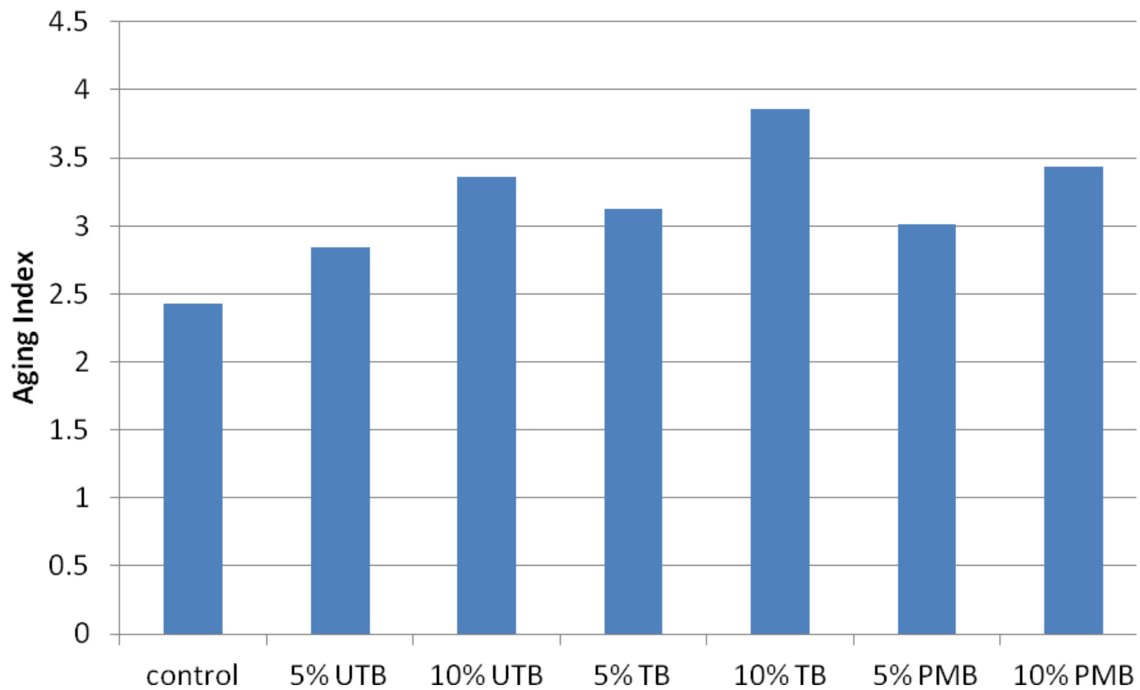


Figure 4-14: Aging Indexes of control binder and bio oil modified asphalt binders in low temperature ranges after RTFO aging

4.3.4 Critical Temperatures for Rutting Characterization

Superpave^{TM} binder specification makes requirement for the $G^*/\sin\delta$ for both virgin asphalt binders and binders after RTFO aging for rutting performance consideration. However, as mentioned before, the rutting normally occurs after the asphalt has experienced the short-term aging, it is more reasonable to specify $G^*/\sin\delta$ only for RTFO aged asphalt binders. The requirement for the RTFO aged asphalt binders to satisfy rutting resistance is $G^*/\sin\delta > 2.2kPa$

at 58°C and 1.59Hz (10rad/s). Based on this, a critical high temperature to meet G*/sinδ>2.2kPa at 1.59Hz can be obtained.

Figure 4-15 shows the critical high temperatures of control asphalt binder and bio oil modified asphalt binders after RTFO aging for the rutting performance consideration. It is found that the critical temperatures of the 5% and 10% UTB modified binders were 1.32°C and 1.48°C higher than the control binder; the 5% and 10% TB modified binders were 1.22°C and 2.69°C higher than the control binder; and the critical temperatures of 5% and 10% PMB modified binders were 1.95°C and 2.32°C higher than that of the control binder.

To compare the critical high temperatures among the three types of bio oil modified asphalt binders, it is observed that the PMB and TB modified asphalt binders obtained higher critical temperature than the UTB modified asphalt binders. This result indicates that with the same percentage of bio oil added into the control binder, PMB and TB modified asphalt binders are expected to gain better rutting performances than the UTB modified asphalt binders.

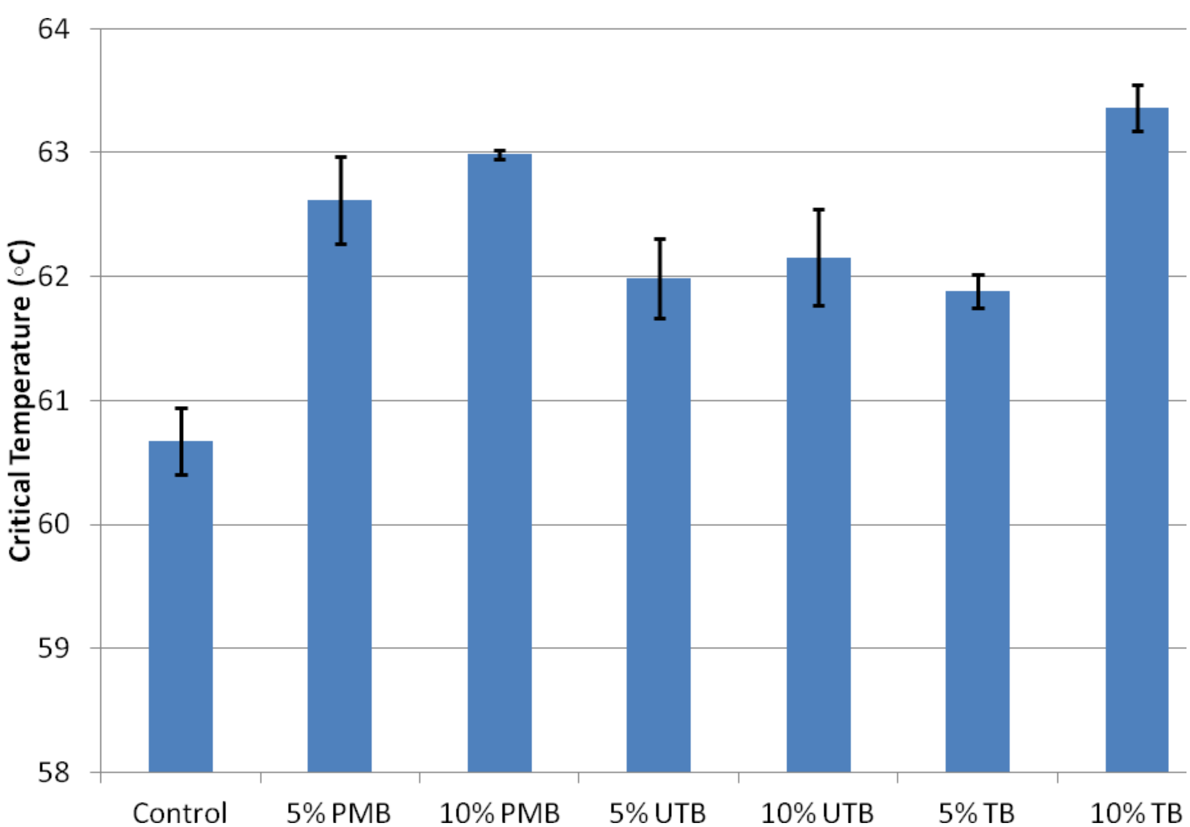


Figure 4-15: Critical high temperatures for control asphalt binder and bio oil modified asphalt binders for rutting consideration

4.3.5 DSR Test for PAV Aged Binders

DSR test for PAV aged asphalt binder is conducted for the fatigue characterization. In this study, DSR test for PAV aged asphalt binders were conducted for control binder and bio oil modified asphalt binders. The temperatures selected for the test were 13°C, 19°C, 25°C, 31°C and 37°C considering that the fatigue normally occur in a medium temperature.

Figure 4-16 to Figure 4-18 display the G* master curves plot for the control asphalt binder and three types of bio oil modified asphalt binders after PAV aging. It is observed that with the increase of bio oil percent in the asphalt binders, the |G*| after PAV aging showed a significant increase. The |G*| of 5% and 10% UTB modified asphalt binders were 186.3% and 267.7% higher than that of the control binder respectively; The |G*| of 5% and 10% TB modified asphalt binders were 180.7% and 215.7% higher than that of the control binder respectively; The |G*| of 5% and 10% PMB modified asphalt binders were 187.1% and 250.7% higher than that of the control binder respectively. Since |G*| after PAV aging is an indicator for fatigue resistance, it is anticipated that the addition of bio oil into the control binder would reduce the fatigue performance.

Superpave™ binder specification has a requirement of the |G*| after PAV aging for PG 58-28 at 19°C and 1.59Hz. The requirement is: $G^* * \sin\delta < 5000$kPa. Table 4-1 illustrates the |G*| of control binder and bio oil modified asphalt binders at 19°C and 1.59 Hz after PAV aging. It is found that although there is a significant increase, all of the bio oil modified asphalt binders can meet the Superpave™ requirement.

To make the comparison among the three types of bio oil modified asphalt binders, it is found that there was no significant difference for the |G*|s among the three types of bio modified asphalt binders after PAV aging.

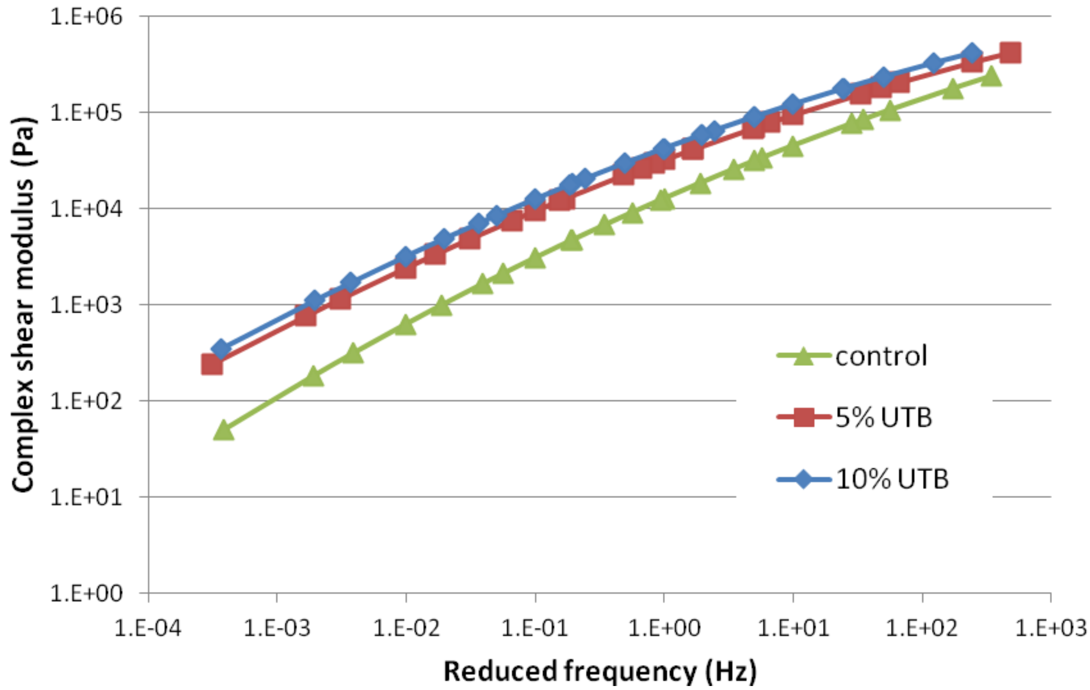


Figure 4-16: G* master curve plot for control binder and 5% and 10% UTB modified asphalt binders after PAV aging

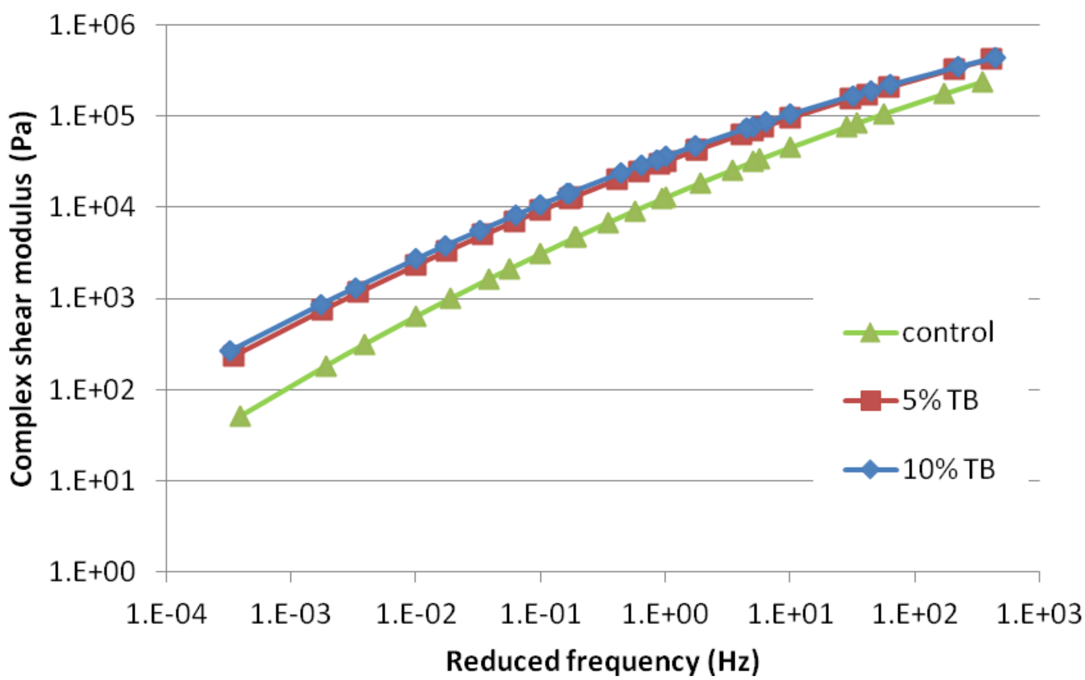


Figure 4-17: G* master curve plot for control binder and 5% and 10% TB modified asphalt binders after PAV aging

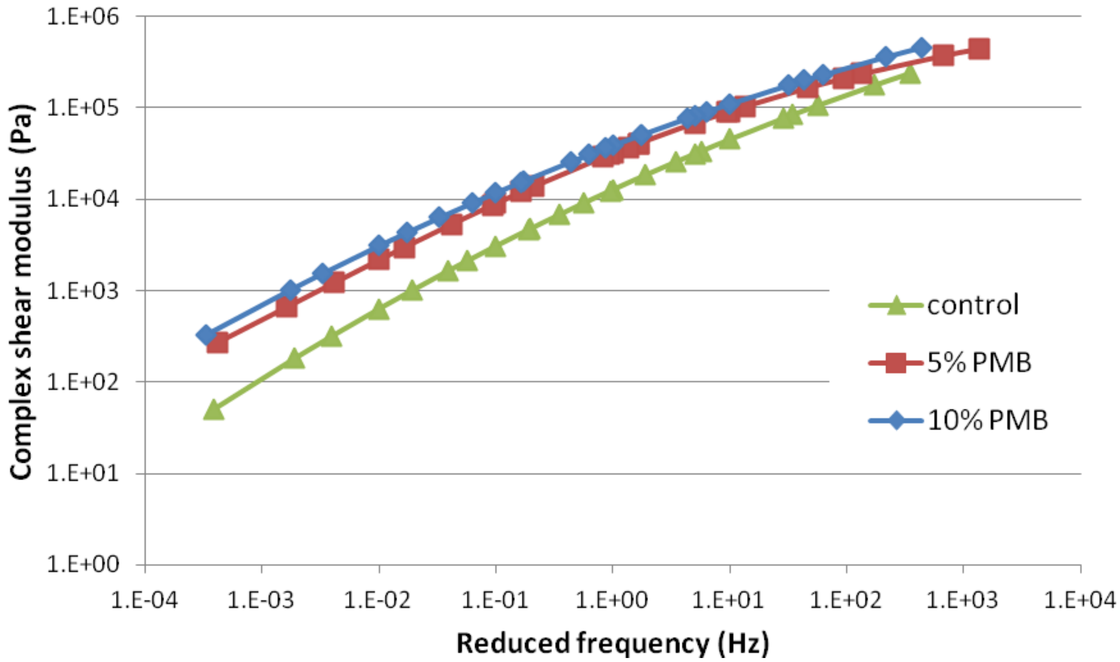


Figure 4-18: G* master curve plot for control binder and 5% and 10% PMB modified asphalt binders after PAV aging

Table 4-1: |G*| of control binder and bio oil modified asphalt binders at 19°C and 1.59Hz after PAV aging

Binder Types	|G*| (kPa)	Pass or Fail Specification
Control	40.9	Pass
5% UTB	93.6	Pass
10% UTB	112.8	Pass
5% TB	91.6	Pass
10% TB	102.0	Pass
5% PMB	89.6	Pass
10% PMB	109.1	Pass

4.4 BBR Test Results

The BBR test was conducted to study the low temperature performances of the control asphalt binder and the bio oil modified asphalt binders. The test temperatures for control binder were -18°C and -24°C while the test temperatures for bio oil modified asphalt binders were -18°C and -

12°C. The creep stiffness and m-value at 60s were obtained. Table 4-2 and Table 4-3 show the creep stiffness and m-value at 60s for control asphalt binder and the three types of bio oil modified asphalt binders at -12°C and -18°C.

It is observed that the creep stiffness of 5% and 10% UTB modified binders were 32.3% and 47.7% higher than that of the control binder at -18°C. The m-value of 5% and 10% UTB modified asphalt binders were 0.19 and 0.60 at -18°C. The creep stiffness of 5% and 10% UTB modified binders were 36.6% and 42.0% higher than that of the control binder at -18°C. The m-values at 60s of 5% and 10% UTB modified asphalt binders were 0.56 and 0.66 lower than that of the control binder at -18°C. The creep stiffness of 5% and 10% PMB modified binders were 45.5% and 56.3% higher than that of the control binder at -18°C. The m-value of 5% and 10% PMB modified asphalt binders at 60s were 0.53 and 0.72 lower than that of the control binder at -18°C.

According to the Superpave^{TM} requirement for PG 58-28, the creep stiffness should be less than 300MPa, and the m-value should be more than 0.3 at -18°C. Based on this, it is found that the both the stiffness value of 5% and 10% UTB modified asphalt binder can meet the requirement of Superpave^{TM} specification. The 5% UTB modified binders can also pass the m-value requirement but the 10% UTB modified asphalt binder failed the m-value requirement. Both the TB and PMB modified asphalt binders met the creep stiffness requirement but failed the m-value requirement.

Since a lower stiffness and higher m-value are thought to bring better low temperature performance, it is concluded that 5% and 10% UTB modification on the base asphalt binder would reduce the low temperature performance of asphalt binders.

Because all of the bio oil modified asphalt binders passed the requirement at -12°C but failed at -18°C, and that the control binder passed the requirement at -18°C but failed at -24°C. The critical low temperatures of the asphalt binders studied were obtained by an interpolation. Figure 4-19 shows the critical low temperatures for control binder and the three types of bio oil modified binders. Compared to control binder, the 5% and 10% UTB modification increased the critical temperature by 0.63 and 3.33°C respectively; 5% and 10% TB modification increased the critical temperature 3.58 and 4.73°C respectively; The 5% and 10% PMB modification increased the critical temperature by 2.62 and 4.32°C respectively.

Since a critical low temperature means the lowest temperature the asphalt binder can resist, the results also showed the addition of bio oil into the control asphalt would impact the low temperature performance.

Table 4-2: Creep stiffness and m-value of 5% and 10% UTB, 5% and 10% TB, and 5% and 10% PMB modified asphalt binder tested at -18°C

Asphalt Binder	Creep stiffness at 60s (MPa)			m-value at 60s		
	Testing value	**specification**	**Pass or fail**	**Testing value**	**specification**	**Pass or fail**
Control	176	<300	Pass	0.347	>0.3	Pass
5% UTB	233.0	<300	Pass	0.328	>0.3	Pass
10% UTB	260	<300	Pass	0.287	>0.3	Fail
5% TB	240.5	<300	Pass	0.291	>0.3	Fail
10% TB	250	<300	Pass	0.281	>0.3	Fail
5% PMB	256	<300	Pass	0.294	>0.3	Fail
10% PMB	275	<300	Pass	0.275	>0.3	Fail

Table 4-3: Creep stiffness and m-value of 5% and 10% UTB, 5% and 10% TB, and 5% and 10% PMB modified asphalt binder tested at -12°C

Asphalt Binder	Creep stiffness at 60s (MPa)	m-value at 60s	Pass or fail
Control	46.4	0.414	Pass
5% UTB	97	0.332	Pass
10% UTB	121	0.369	Pass
5% TB	92.8	0.337	Pass
10% TB	103	0.330	Pass
5% PMB	108.9	0.375	Pass
10% PMB	122	0.348	Pass

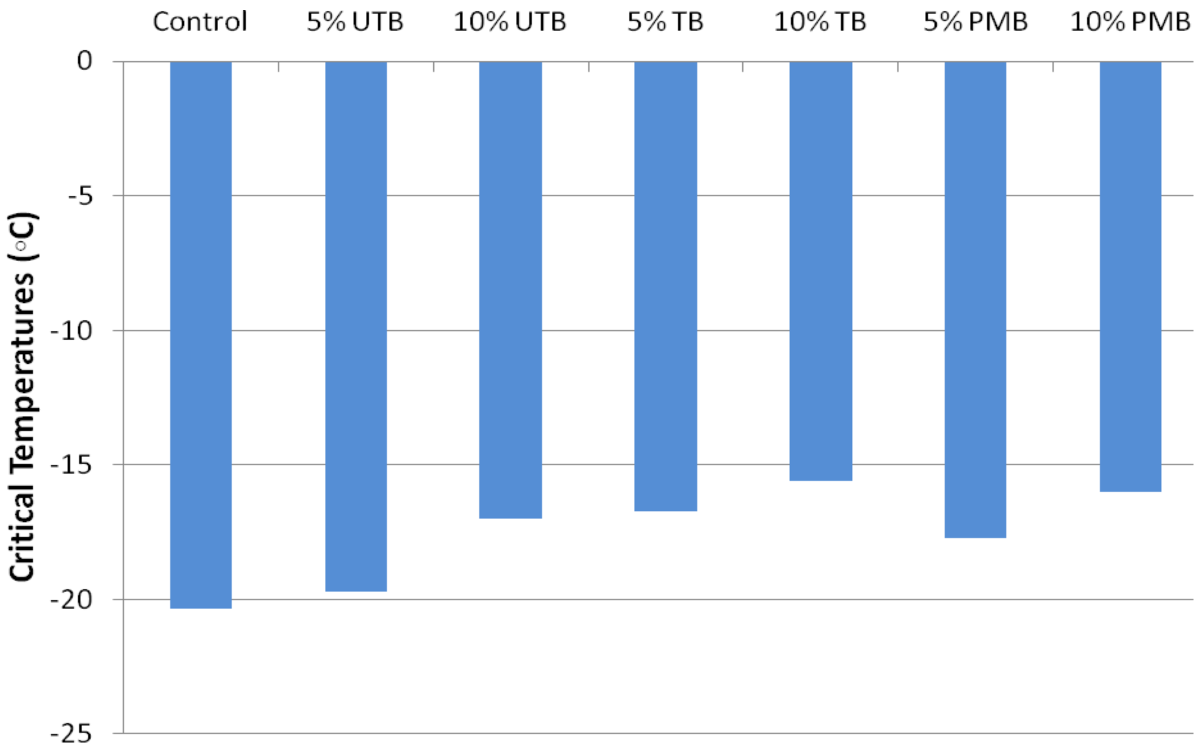


Figure 4-19: Critical low temperatures of control binder and the three types of bio oil modified asphalt binders obtained from BBR test

To sum up the BBR test results for three types of bio oil modified asphalt binders, the addition of bio oil increased the creep stiffness and decreased the m-value at 60s during the test, which caused an increase of the critical temperature. This indicates that the addition of bio oil into the base asphalt PG 58-28 results decreased the low temperature performance.

4.5 Summary of Findings

The rheological properties of asphalt binder PG 58-28 and UTB, TB and PMB modified asphalt binders were studied, and the summaries of finding are presented as below:

1) The viscosity of the bio oil modified asphalt binder is lower than that of the control asphalt binder before RTFO aging but is higher than that of the control binder after RTFO aging due to the fast aging of bio oil;
2) With the increase of bio oil percentage in the asphalt binder, the aging index also increases. This is consistent with previous studies on bio oil aging. In addition, TB

modified asphalt binder shows higher aging index than UTB and PMB modified asphalt binders during short-term aging;

3) Bio oil modified asphalt binders have higher complex shear modulus (|G*|) and higher critical high temperature than the control binder after standard RTFO aging, which indicates that the bio oil modified asphalt binders can obtain better high temperature performance than the control binder;
4) The addition of bio oil brings a significant |G*| increase after PAV aging compared to the control binder in medium temperature range, which indicates that the addition of bio oil reduces the fatigue performance;
5) The addition of bio oil would increase the creep stiffness, reduce the m-value in low temperature ranges and hence increases the critical low temperature according to Superpave^{TM} binder test specification, which makes the asphalt binder more susceptible to thermal cracking.

CHAPTER 5: EVALUATION OF THE RHEOLOGICAL PROPERTIES OF ASPHALT BINDERS PARTIALLY REPLACED BY BIO OIL

5.1 Introduction

Since bio oil is a sustainable material that has wide application potential in the future, it is necessary to study the properties of asphalt binders containing high percentage of bio oils. In another word, bio oil would serve as an extender instead of a modifier as investigated in Chapter 4. In this chapter, 10%, 30%, 70% and 100% bio oil blended asphalt binders are prepared and the rheological properties are studied by RV test, RTFO test, PAV test, DSR test and BBR test. The bio oil and control asphalt binder were mixed by the high shear mixer for 15 minutes at 110°C.

5.2 RV Test Results

5.2.1 RV Test for Virgin Binders

The RV test was conducted on control asphalt binder PG 58-28, 10%, 30%, 70% and 100% bio oil blended asphalt binders to study the rheological properties of asphalt binders in high temperature ranges. Metwally and Williams (Metwally and Williams 2010) pointed that the pure bio oil cannot be treated at temperature higher than 120°C. As a result, the temperatures selected for the bio oil blended asphalt binders were 90°C, 100°C, 110°C, 120°C, 130°C and 140°C.

Figure 5-1 illustrates the RV test results for UTB blended asphalt binders in the temperature range 90°C to 140°C. It is found that with the increase of the UTB percent in the asphalt binder, the rotational viscosities decreased overall except the 30% UTB blended asphalt binder. The rotational viscosities of 10%, 70% and 100% UTB blended asphalt binder were 9.35%, 33.6% and 71.0% lower than that of the control binder. However, the viscosities of 30% UTB blended asphalt was 44.3% higher than that the control binder, which was unexpected. To prevent the over aging of bio oil during the mixing, one more 30% UTB blended asphalt binders was prepared by hand at 100°C. However, the RV test result was similar. Table 5-1 shows the RV test results for the 30% UTM blended asphalt binders mixed by high shear mixer and by hand. It is found that the rotational viscosity of UTB bioasphalt mixed by hand was even slightly higher than that of the bioasphalt mixed by high shear mixer.

In addition, it is also observed from Figure 5-1 that the 70% and 100% bioasphalt showed an increase trend at 140°C. This was mainly because of the chemical reaction inside the bio oil that generated new chemicals and made the bioasphalt stiffer.

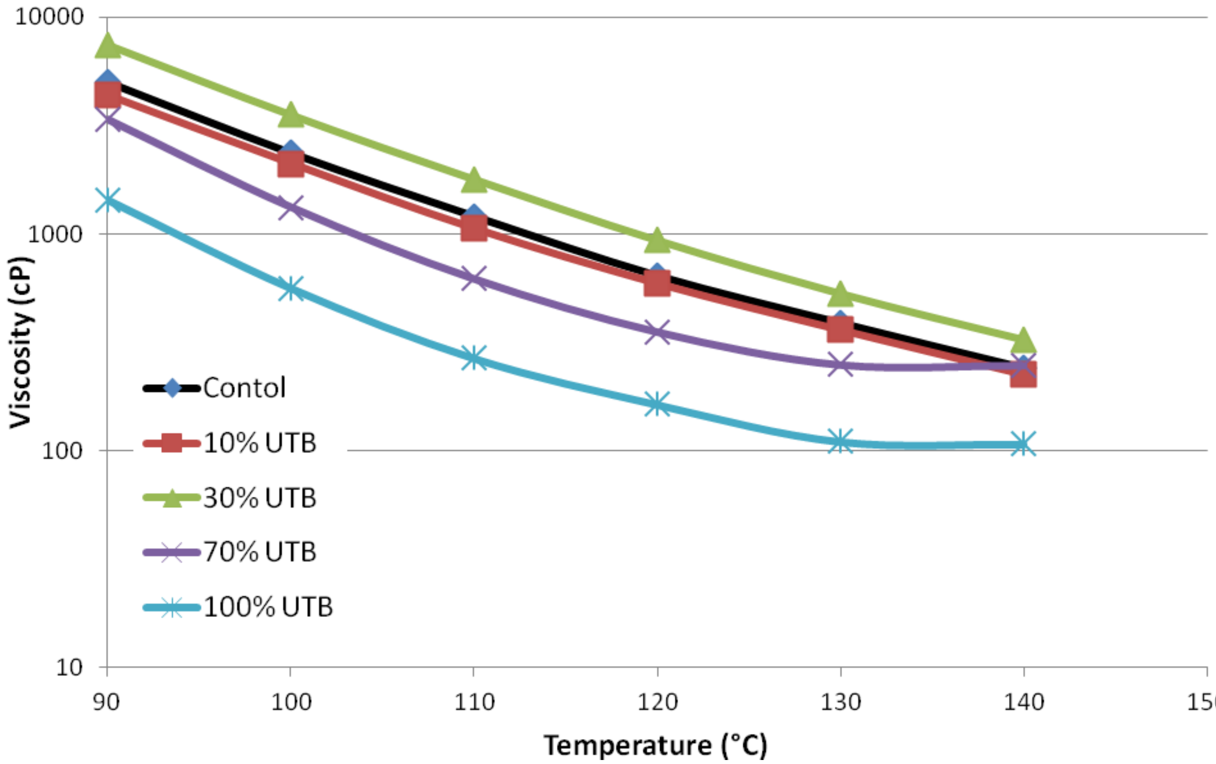


Figure 5-1: RV test results for control binder, 10%, 30%, 70% and 100% UTB bioasphalt binders

Table 5-1: The viscosity comparison of 70% UTB blended asphalt binders mixed by high shear mixer and by hand

sample		90°C	100°C	110°C	120°C	130°C	140°C
Mixing by high shear mixer at 110°C	Sample #1	7357	3500	1770	916	525	321
	Sample #2	7562	3597	1812	955	538	330
	Average	**7468.5**	**3548**	**1791**	**936**	**531**	**325**
Mixing by hand at 110°C	Sample #1	9444	4388	2125	1125	605	366
	Sample #2	9166	4250	2062	1016	580	342
	Average	**9305**	**4319**	**2093**	**1070**	**592**	**354**

Figure 5-2 shows the RV test results of the control binder, 10%, 30%, 70% and 100% TB bioasphalt binders. It is found that with the increase of bio oil percentage, the rotational viscosity decreased overall. The viscosities of 10%, 30%, 70% and 100% TB bioasphalt binders were 8.3%, 20.7%, 42.3% and 60.0% lower than the control asphalt binder respectively in average.

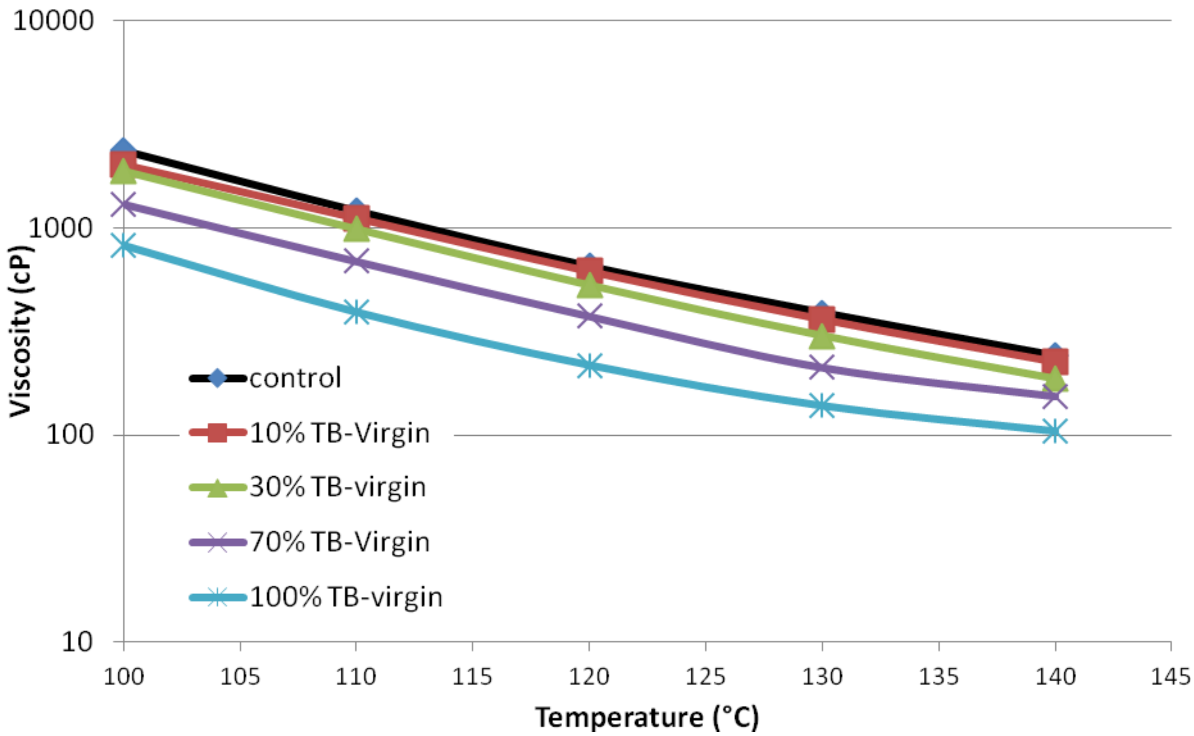


Figure 5-2: RV test results for control asphalt binder, 10%, 30%, 70% and 100% bioasphalt binders

Figure 5-3 shows the RV test results for control binder, 10%, 30%, 70% and 100% PMB bioasphalt binders. Based on the test results, it is found that the rotational viscosities of 10% and 100% PMB blended binders were 13.2% and 26.9% lower than the control binder in average. However, the rotational viscosities of 30% and 70% PMB blended asphalt binders were 21.3% and 316.7% higher than the control binder. The testing results were a little strange. One more 30% and 70% PMB blended asphalt binder mixed by hand at temperature 100°C to avoid the over aging. However, there was not a significant different for the test results.

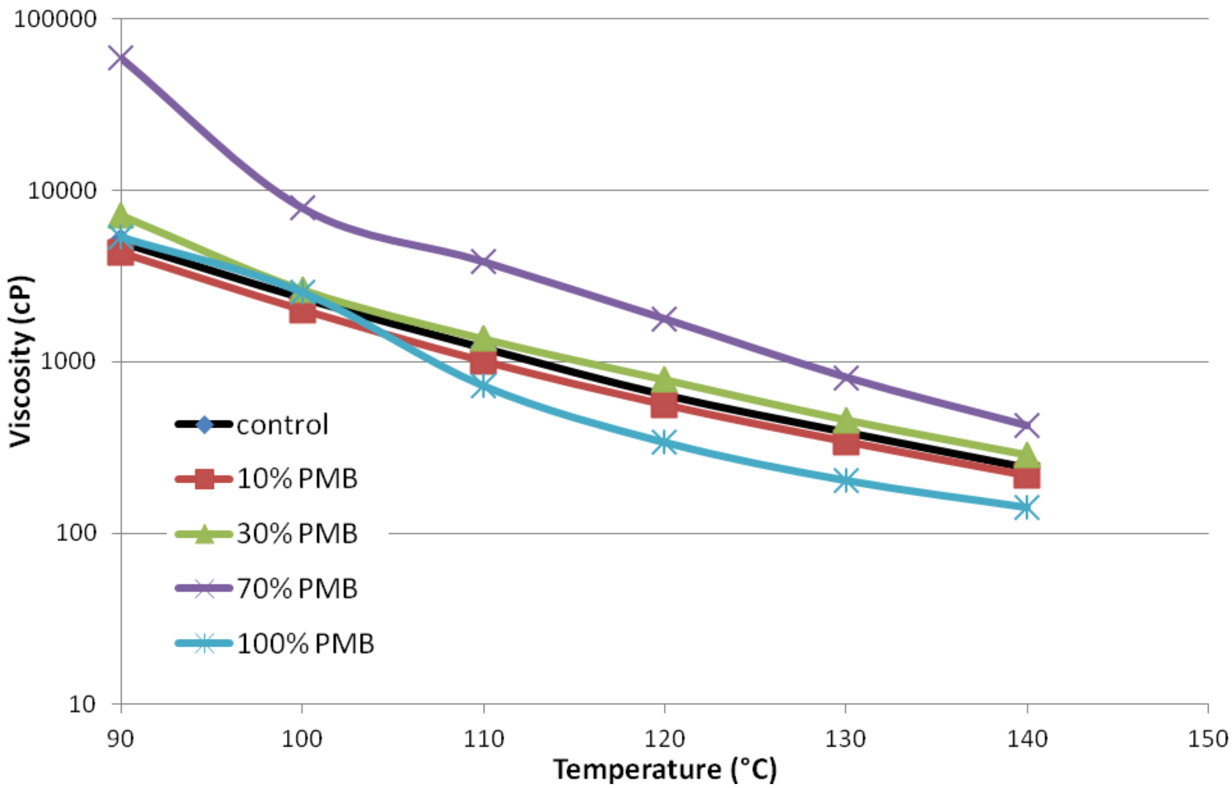


Figure 5-3: RV results for control asphalt binder, 10%, 30%, 70% and 100% PMB bioasphalt binders

To sum up the findings, it is found that: 1) all of the three pure bio oils were softer than the control binder PG 58-28 in the temperature range 90°C to 140°C; 2) PMB bioasphalt showed higher viscosities than the UTB and TB bioasphalt; 3) with the increase of bio oil percentage in the bioasphalt, there was a good decrease trend for the TB bioasphalt while the trends of UTB and PMB bioasphalt were unexpected.

5.2.2 RV Test Results for RTFO Aged Binders

RV test for RTFO aged binders can study the effect of short-term aging on the rheological properties of asphalt binders in high temperature ranges. The RTFO test for high percent bio oil blended asphalt binders was modified as proposed by Metwally and Williams (Metwally and Williams 2010). In the modified RTFO test, the aging temperature was 120°C and aging time was 20 minutes. Figure 5-4 shows the RV test results for control binder, 10%, 30% and 70% UTB bioasphalt binders after RTFO aging. It is observed that the rotational viscosities of the 10%, 30% and 70% UTB bioasphalt binders were -1.9%, 51.3% and 322.9% higher than that of the control binder. The overall trend was as expected for the aging of bio oil is much quicker than the base asphalt. For the 10% UTB bioasphalt binder, considering that the viscosity of virgin 10% UTB bioasphalt binder was 9.4% lower the control binder, it indicates that the aging of 10% UTB blended asphalt binder was still higher than that of the control. The higher aging behavior can be attributed to the occurrence of polymerization reactions between the 15 molecular compounds and the oxidative (oxygen-related aging) hardening in the presence of air.

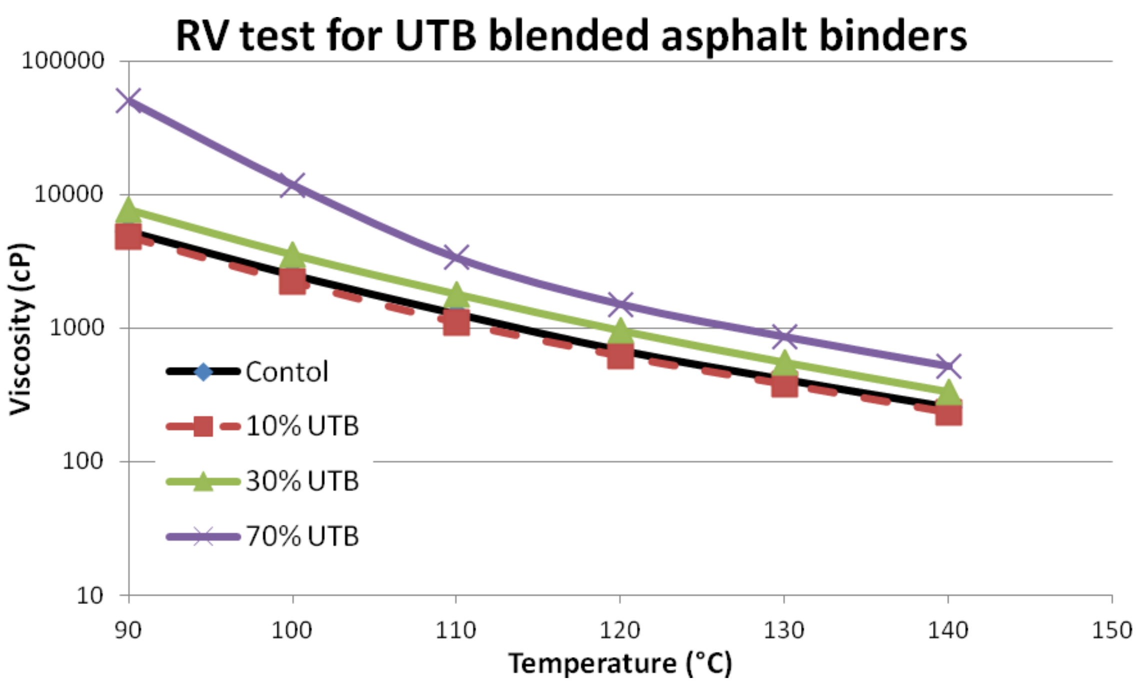


Figure 5-4: RV results for control asphalt binder PG 58-28, and 10%, 30%, 70% and 100% UTB bioasphalt binders after RTFO aging

Figure 5-5 shows the RV test results for control binder, 10%, 30% and 70% TB blended asphalt binders after RTFO aging. Based on the test results, it is observed that the rotational viscosity of 10%, 30% and 70% TB blended asphalt binders were -0.6%, 40.6% and 290.9% higher than that of the control binder. This means that with the increase of the TB percent in the bioasphalt binders, the rotational viscosity increased rapidly. The result was mainly due to the fast aging of bio oil.

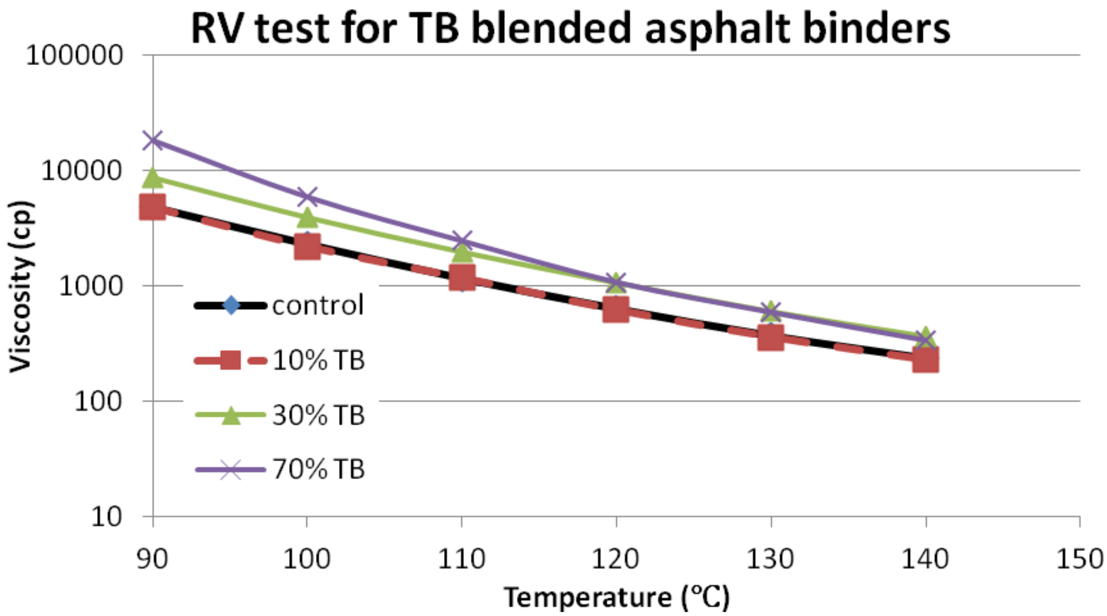


Figure 5-5:RV results for control asphalt binder PG 58-28, and 10%, 30%, 70% and 100% TB bioasphalt binders

Figure 5-6 shows the RV test results of control binder PG 58-28, 10%, 30% and 70% PMB blended asphalt binders after RTFO aging simulation. It is observed that the rotational viscosities of 10%, 30% and 70% PMB blended asphalt binder were -5.5%, 25.0% and 346.8% higher than that of the control.

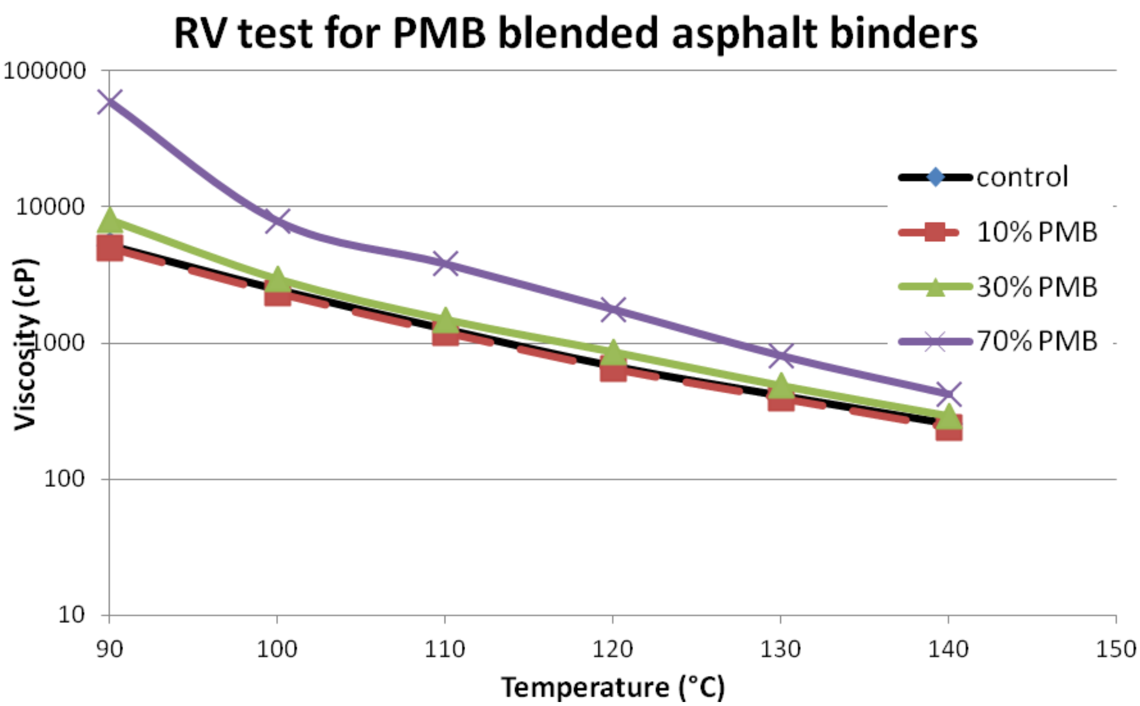


Figure 5-6: RV results for control asphalt binder PG 58-28, and 10%, 30%, 70% and 100% PMB bioasphalt binders

5.3 DSR Test Results

5.3.1 DSR Test Results for Virgin Asphalt Binders

Figure 5-7 showed the |G*| master curve plot for the virgin control binder, 10%, 30% and 70% UTB bioasphalt binders. It is observed that 30% UTB blended asphalt binder showed the highest |G*|, followed by 10% UTB bio asphalt binder and the control binder. 70% UTB bio asphalt showed the lowest |G*|. The test results were consistent with the rotational viscosity results. The 10%, 30% and 70% UTB blended asphalt binders showed 9.5%, 52.1% and -17.7% higher than that of the control binder in average.

Superpave^{TM} specification recommends G*/sinδ value at 58°C and 1.59Hz for PG 58-28. Based on this, the G*/sinδ were obtained and shown in Figure 5-8. It is found that the G*/sinδ of the 30% UTB bioasphalt was highest, followed by that of control binder, 10% and 70% bioasphalt binders.

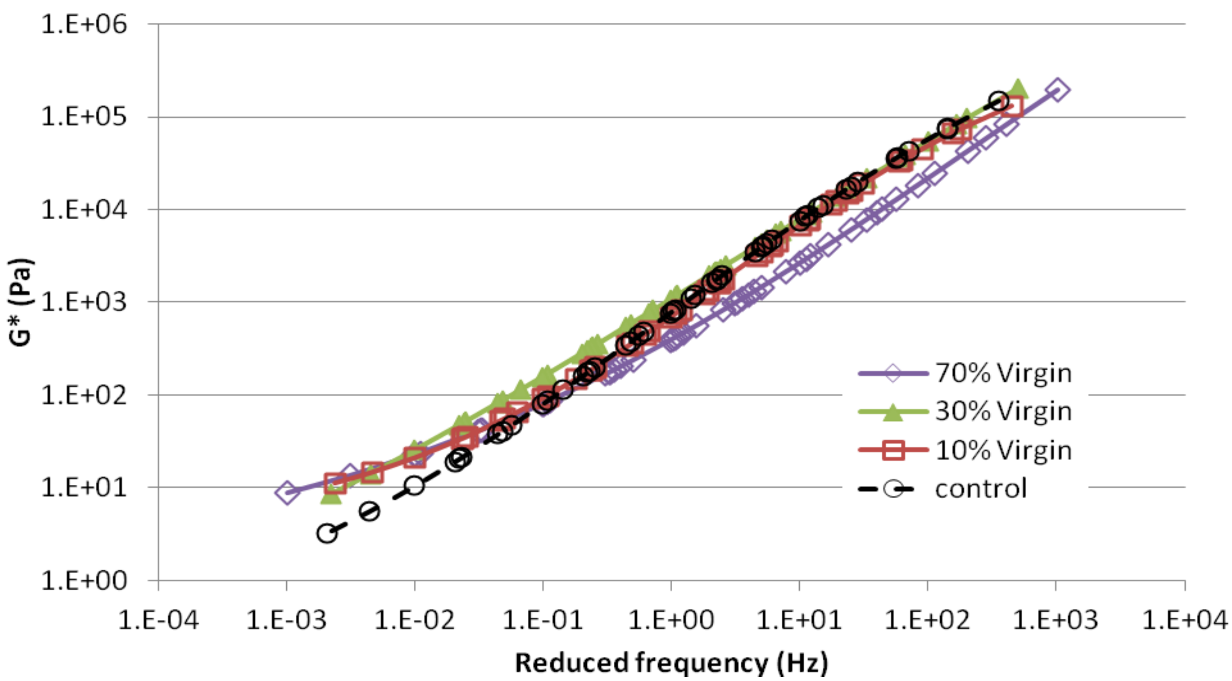


Figure 5-7: Master curve plot for the virgin control binder, 10%, 30% and 70% UTB blended asphalt binders in temperature range 40°C to 70°C

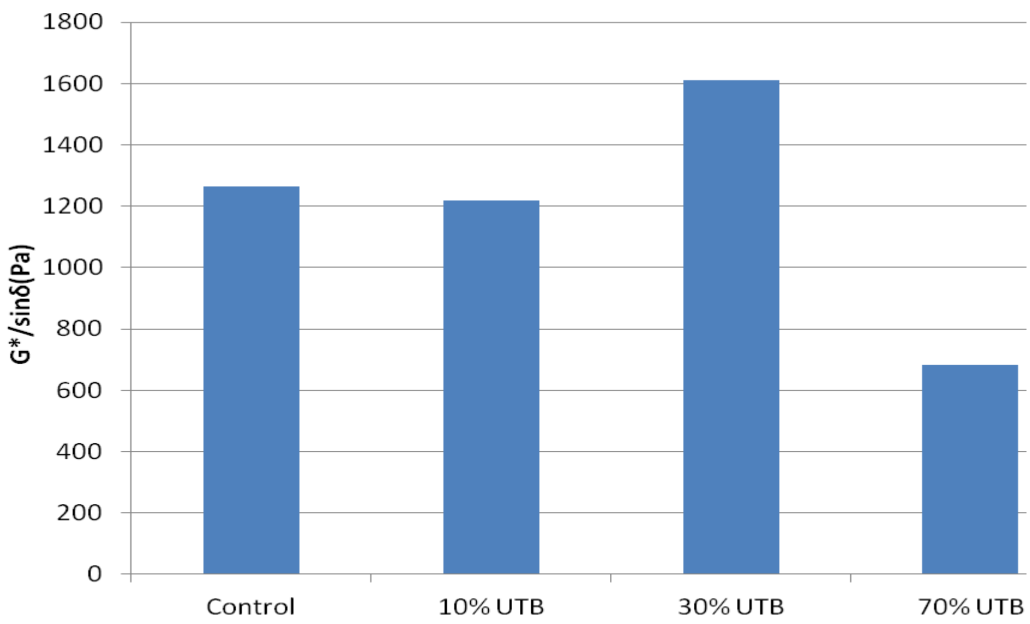


Figure 5-8: G*/sinδ values of control binder, 10%, 30% and 70% UTB bioasphalt at 58°C and 1.59Hz

Figure 5-9 shows the predicted master curve for |G*| of control asphalt binder, 10%, 30%, 70% and 100% TB blended bioasphalt binders. Similar as the UTB blended asphalt binder, it is found that in the low reduced frequency are the |G*| of 10%, 30%, 70% and 100% TB blended asphalt binders were higher than that of the control binder PG 58-28. However, in the high reduced frequency area, the |G*| shows a decrease trend with the increase of bio oil percent overall. The |G*|s of 30%, 70% and 100% virgin bio asphalt are 13%, 22% and 45% lower than that of control asphalt binder in average. This indicates that the virgin bio oil is softer than control binder in the temperature range of 40°C to 70°C. But the TB blended asphalt binders are expected to have better rutting performance based on the higher complex shear modulus in low reduced frequency area.

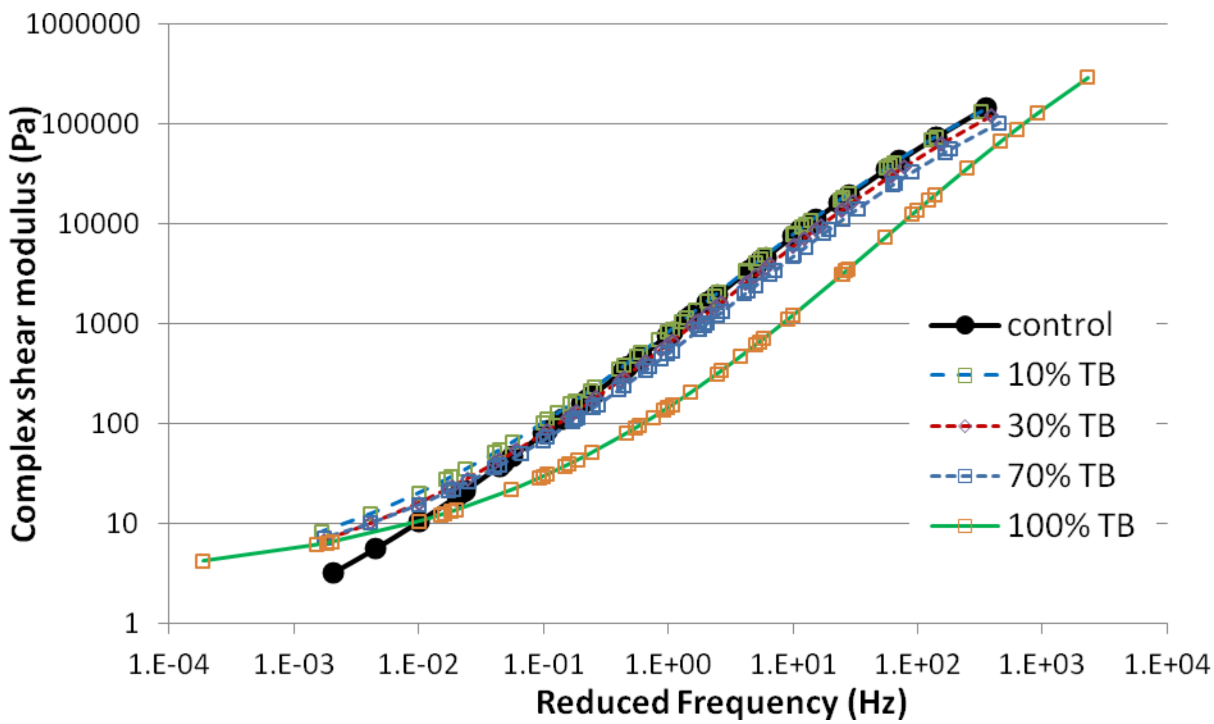


Figure 5-9: Master curve plot for control binder, 10%, 30% and 70% TB bioasphalt binders in the temperature range of 40°C to 70°C.

Figure 5-10 shows the |G*| master curve plot for control binder, 10%, 30%, 70% and 100% PMB bio asphalt binder before RTFO aging at the temperature range of 40°C to 70°C. It is found the 70% bioasphalt showed the highest |G*|, followed by 30%, 100%, 10% bioasphalt and control binder. This trend is similar as that of the RV test results except the 100% bioasphalt, which showed a lower viscosity than the control binder. The |G*| of 10%, 30%, 70% and 100% bioasphalt were 5.8%, 89.4%, 197.2% and 45.2% higher than that of the control binder. This means that the PMB bioasphalt is stiffer than the control binder in temperature range 40°C to 70°C. In addition, since G* is a rutting performance indicator for asphalt mixture, it is expected that the PMB bioasphalt would have better rutting performance than the control binder.

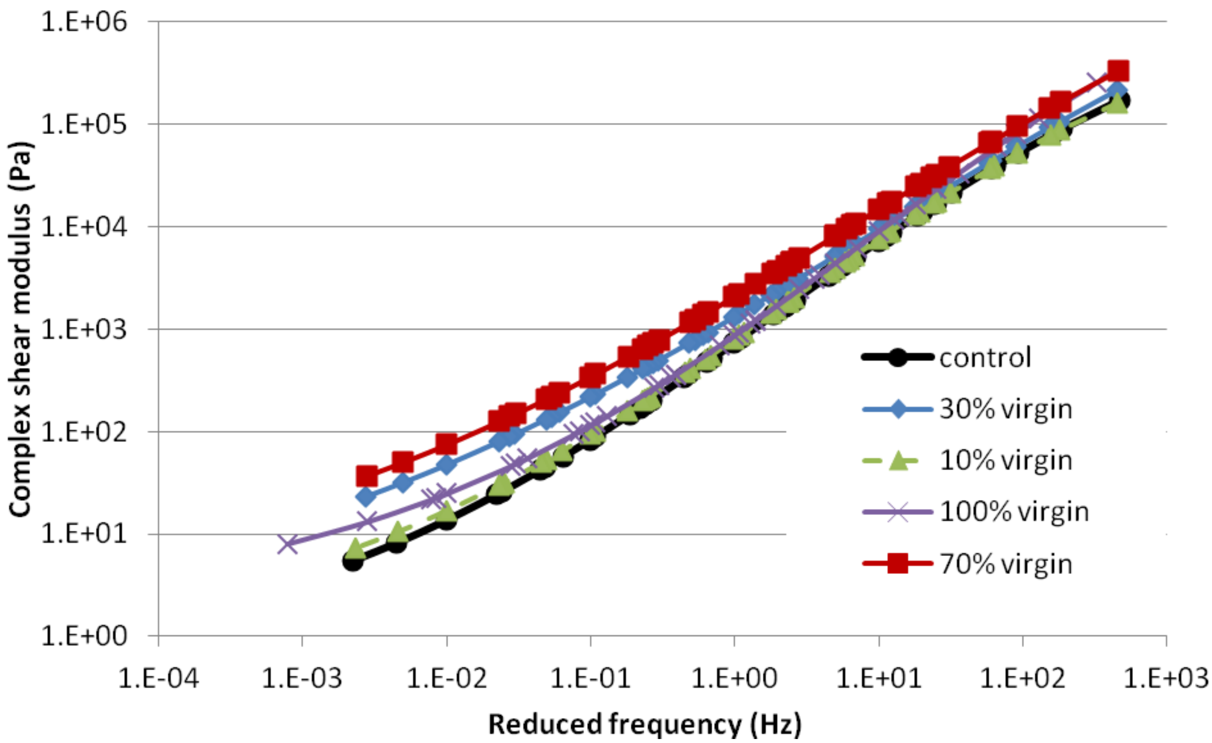


Figure 5-10: Master curve plot for control binder, 10%, 30% and 70% PMB blended asphalt binders before RTFO aging in the temperature range of 40°C to 70°C.

5.3.2 DSR Test for RTFO Aged Asphalt Binders

As mentioned before, the RTFO aging simulation in this study was conducted following the modified testing procedure specified by Williams. The aging condition was changed to 120°C for 20 minutes from 163°C for 85 minutes to avoid over aging of the bio oil. The control asphalt binder, 10%, 30% and 70% bio oil blended asphalt binder after RTFO aging simulation were conducted for the DSR test. Figure 5-11 displays the master curve plot for control binder, 10%, 30% and 70% UTB blended asphalt binders at the temperature range of 40°C to 70°C. It is observed that with the increase of UTB percentage of the asphalt binder, the |G*| showed a increasing trend overall. The |G*|s of 10%, 30% and 70% UTB blended asphalt binders were 8.6%, 26.7% and 438.1% higher than that of the control binder in average respectively in the temperature range 40°C to 70°C. Because the rutting normally occurs after the placement of the HMA mixture, when the asphalt binder has experienced the short-term aging, it is more reasonable to use the |G*|/sinδ after RTFO aging to indicate the rutting performance of HMA mixture. Hence, based on the testing results, it is expected that with the increase of UTB percentage of the asphalt binder, the rutting performance is also expected to increase.

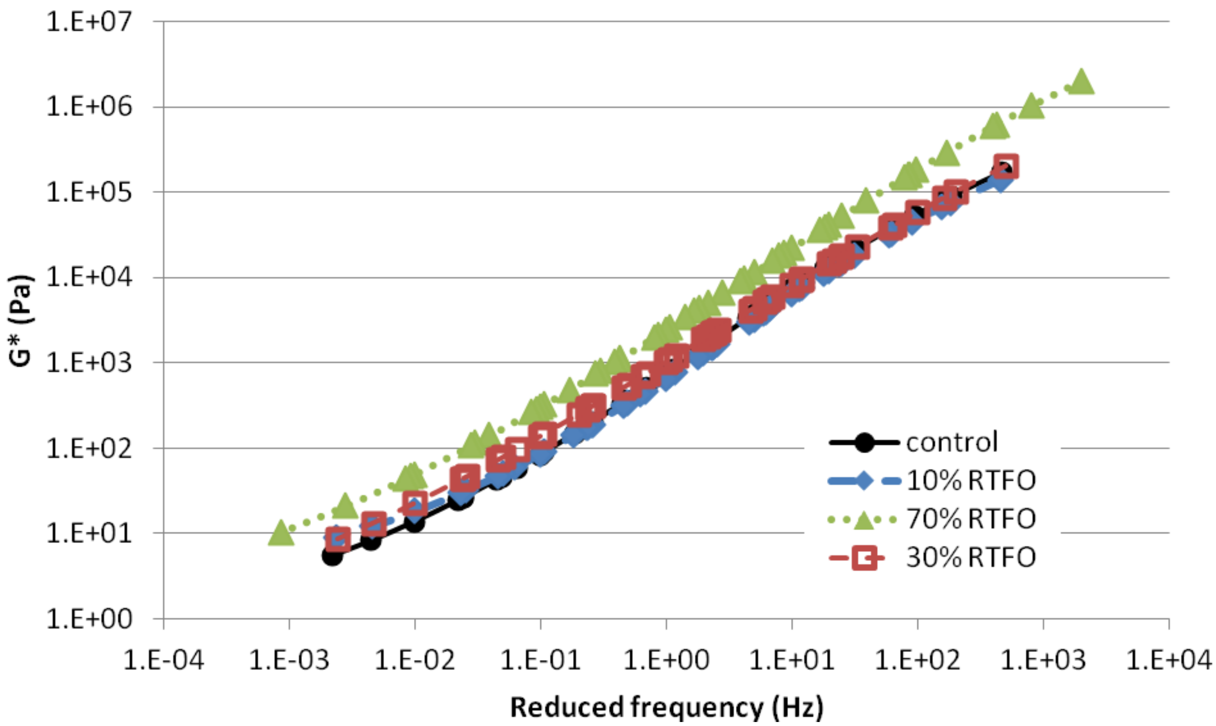
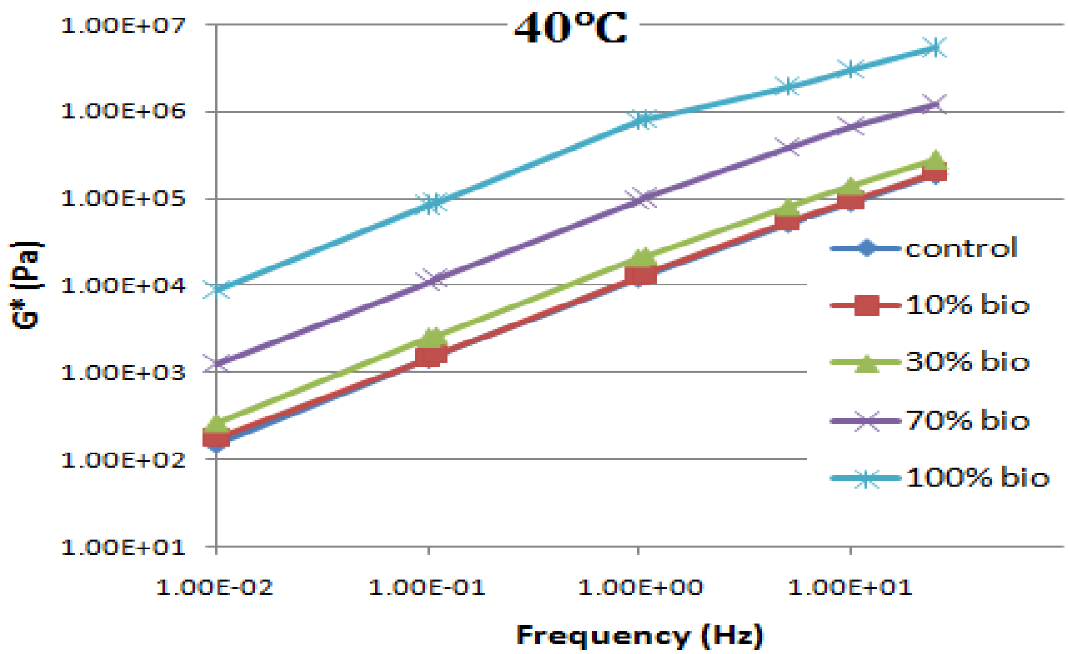


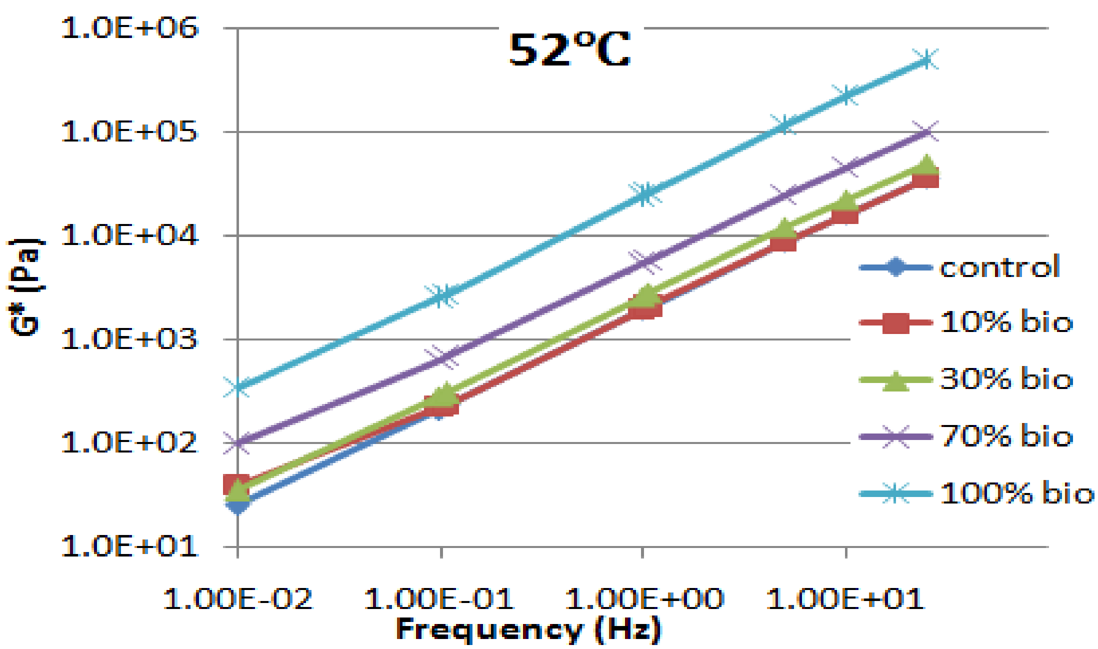
Figure 5-11: Master curve plot for control binder, 10%, 30% and 70% UTB blended asphalt binders in the temperature range of 40°C to 70°C after RTFO aging

Figure 5-12 displays the master curve plot for control binder, 10%, 30% and 70% TB blended asphalt binders in the temperature ranges of 40°C to 70°C after RTFO aging. Based on the testing results, it is found that different from the testing results for virgin binder, with the increase of bio oil percent, the |G*| increased. This is mainly resulting from the faster aging of bio oil in the asphalt binders.



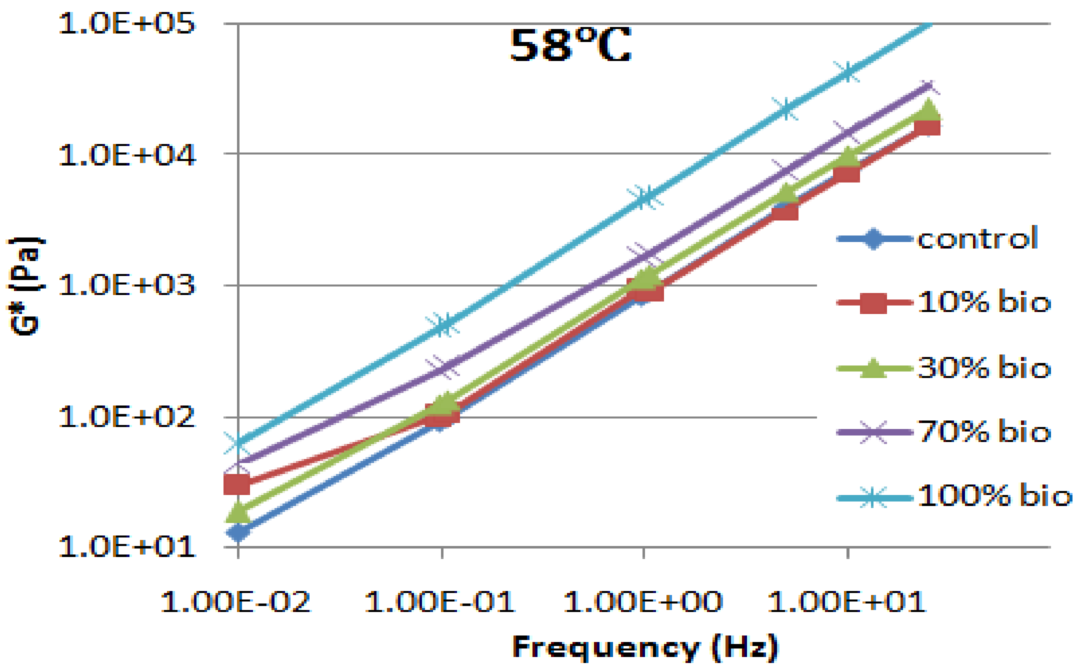
40°C
G* (Pa)
1.00E+07
1.00E+06
1.00E+05
1.00E+04
1.00E+03
1.00E+02
1.00E+01
1.00E-02
1.00E-01
1.00E+00
1.00E+01
Frequency (Hz)
control
10% bio
30% bio
70% bio
100% bio

(a)

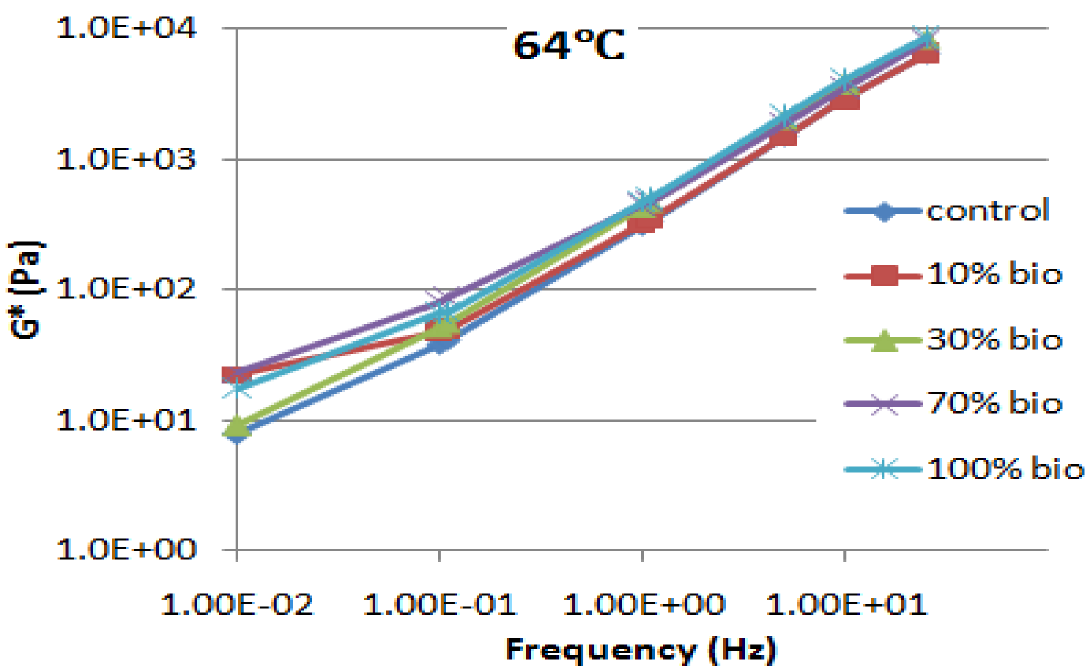


52°C
G* (Pa)
1.0E+06
1.0E+05
1.0E+04
1.0E+03
1.0E+02
1.0E+01
1.00E-02
1.00E-01
1.00E+00
1.00E+01
Frequency (Hz)
control
10% bio
30% bio
70% bio
100% bio

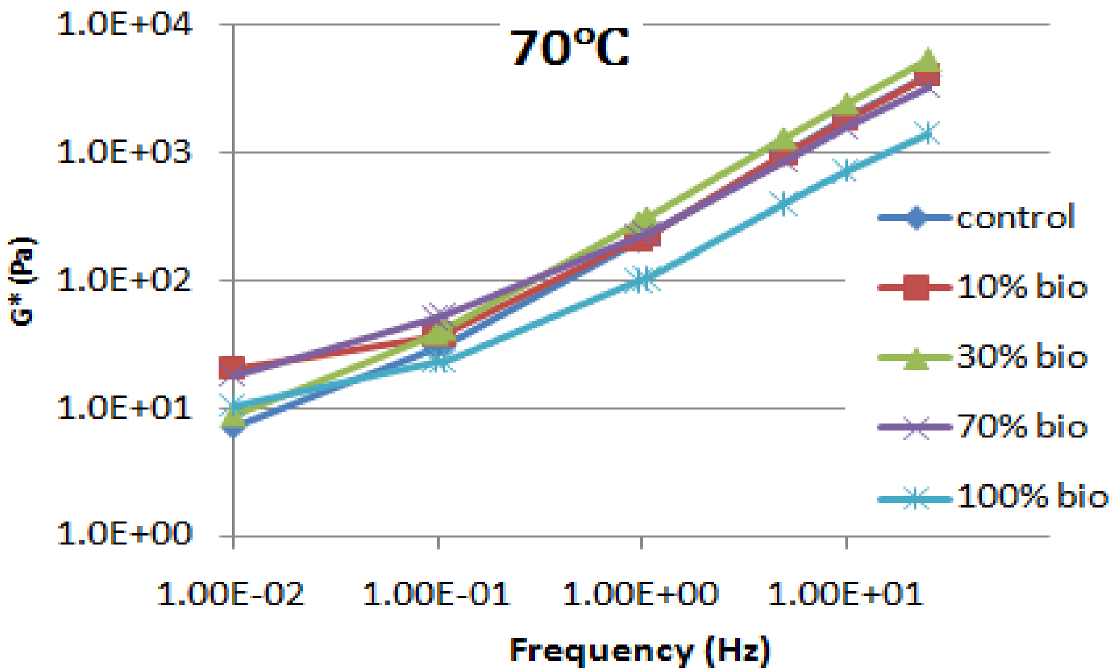
(c)


58ºC
1.0E+05
1.0E+04
1.0E+03
1.0E+02
1.0E+01
G* (Pa)
1.00E-02
1.00E-01
1.00E+00
1.00E+01
Frequency (Hz)
control
10% bio
30% bio
70% bio
100% bio

(d)


64ºC
1.0E+04
1.0E+03
1.0E+02
1.0E+01
1.0E+00
G* (Pa)
1.00E-02
1.00E-01
1.00E+00
1.00E+01
Frequency (Hz)
control
10% bio
30% bio
70% bio
100% bio

(e)



(f)

Figure 5-12: Complex shear modulus (|G*|) of different asphalt binders at temperatures from 40°C to 70°C

However, it should be noticed that the complex moduli of high percent bio asphalt decreased very fast at 64°C and 70°C. After observation during the RTFO test, the research team thought it is because the water eroded the bio oil and penetrated inside the bio oil samples which make a reduction of the tested shear modulus since water has a very low shear modulus. To verify this hypothesis, a mass loss test was conducted for pure bio oils.

A master curve was constructed based on the results at temperatures from 40°C to 58°C, as shown in Figure 5-13. Complex shear moduli of 10%, 30%, 70% and 100% RTFO aged bio asphalt were 9.1%, 43.9%, 329.0% and 2243% higher than the control binder. The sharp increase of |G*| mainly result from the fast aging of bio oil.

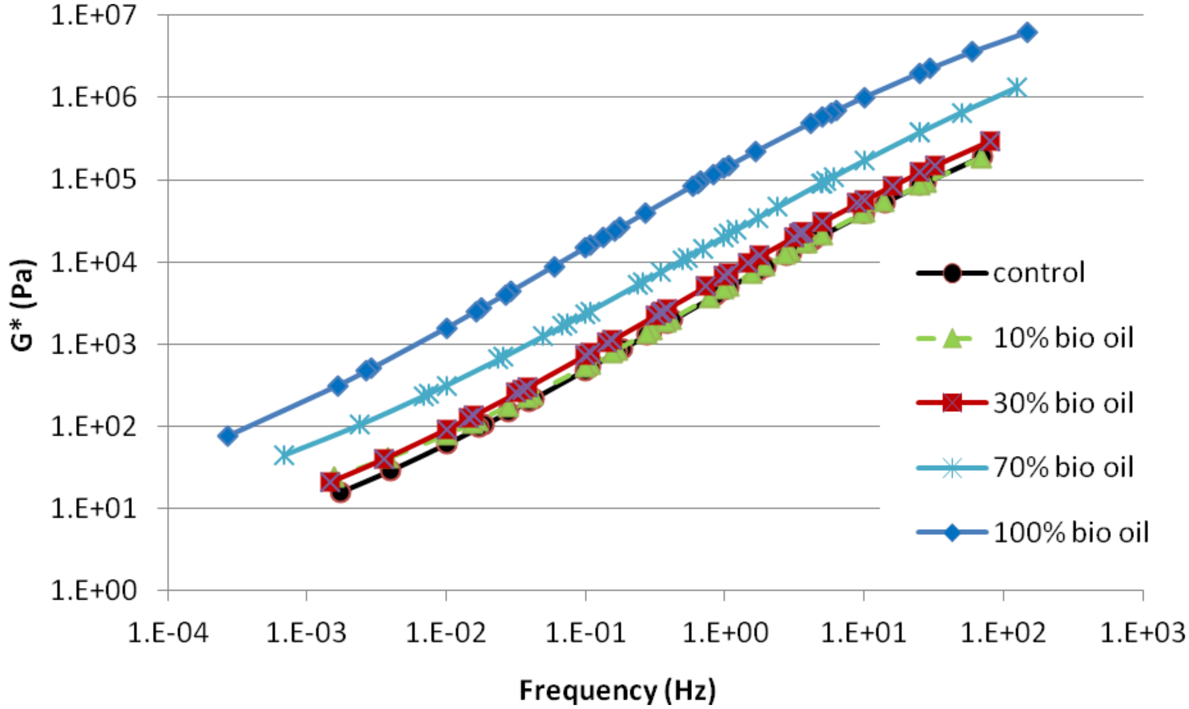


Figure 5-13: Master curve plot for RTFO aged samples of control binder, 10%, 30%, 70% and 100% bio oil blended asphalt binders

Figure 5-14 illustrates the |G*| master curve for control binder, 10%, 30%, and 70% PMB bioasphalt binders after RTFO aging In the temperature range of 40°C to 70°C. It is observed that with the increase of PMB percent in the bioasphalt binders, the |G*| also increased. The |G*| of 10%, 30% and 70% PMB bioasphalt were 30.6%, 100.3% and 372.9% higher than that of the control binder. This also indicates that the addition of PMB in the bioasphalt would enhance the rutting performance.

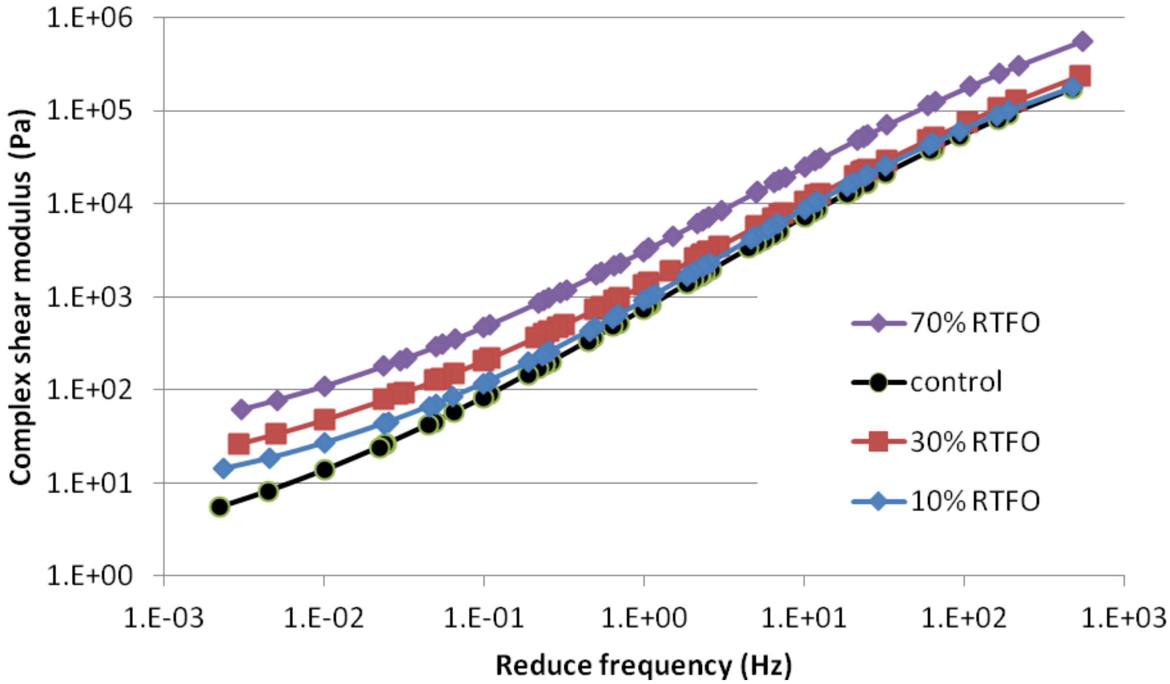


Figure 5-14: Master curve plot for control binder, 10%, 30% and 70% PMB bioasphalt binders after RTFO aging

5.3.3 Aging Indexes of Bio Asphalt Binders

The aging factor of asphalt binder is defined as the ratio of the complex shear modulus after and before the aging. Figure 5-15 shows the relationship between the aging factors and the bio oil percent of the bioasphalt binders in temperature range of 40°C to 70°C. Because bio oil ages much faster than the control binder, it is expected that the aging index increase with the increase of bio oil percentage. However, as seen in Figure 5-15, only the TB bioasphalt showed a good increase trend while the trend of UTB and PMB bioasphalt were a little strange. There are two possible reasons for this: 1) 30% UTB bioasphalt, 30% PMB bioasphalt and 70% PMB bioasphalt had been over aged during the mixing or before mixing because bio oil bottle need to be reheated to take bio oil out; 2) there is some reaction between bio oil and control asphalt binder that made the bioasphalt stiffer and reduced the aging effect. The research team will verify the possible reasons in the future because currently there is no fresh bio oil left.

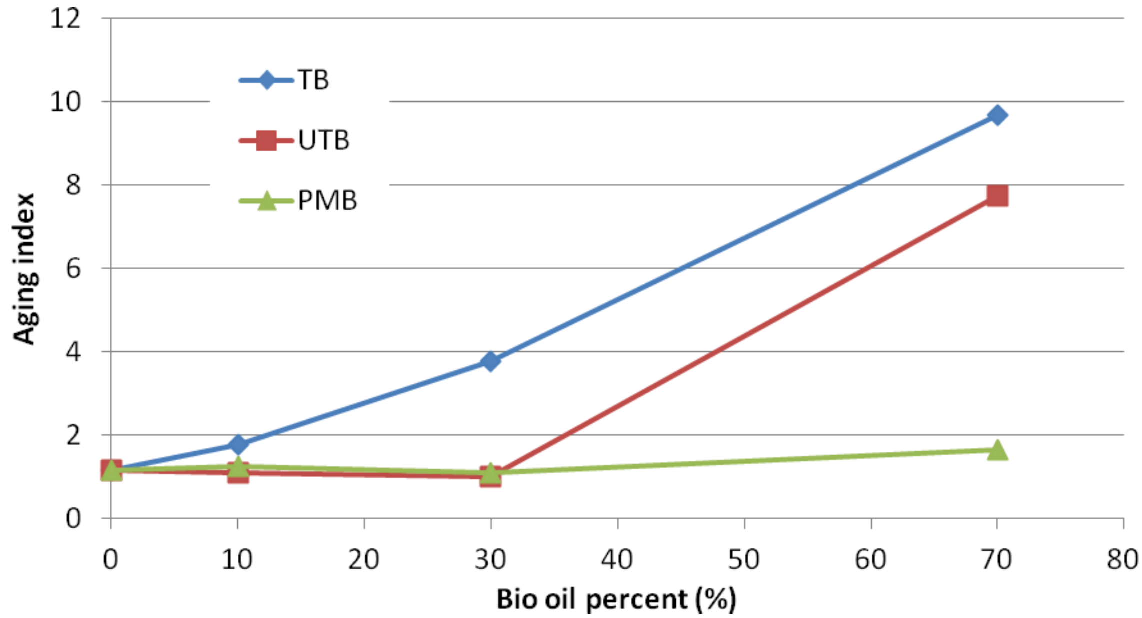


Figure 5-15: Aging indexes of control binder, 10%, 30% and 70% bioasphalt binders after RTFO aging in temperature range of 40°C to 70°C

5.4 BBR Test Results

The samples for BBR test were the asphalt binders after the modified RTFO test and modified PAV test as mentioned before. The test condition was -18°C. Figure 5-16 and Figure 5-17 show the BBR test results for control binder, 10%, 30% and 70% UTB blended asphalt binders. It is observed that with the increase of UTB percent in the asphalt binder, the creep stiffness increase. The creep stiffness at 60s of 10%, 30% and 70% UTB blended asphalt binders were 17.1%, 52.3% and 194.7% higher than the control binder respectively. With the increase of the UTB percent, the m-value decreased overall except that the m-value of 10% UTB was a little higher than that of the control binder. Since a lower creep stiffness and higher m-value are preferred to resist deformation and provide high rate of stiffness change verse time, it is expected that the low temperature performance of control binder and 10% UTB bioasphalt are better than that of 30% and 70% UTB bioasphalt.

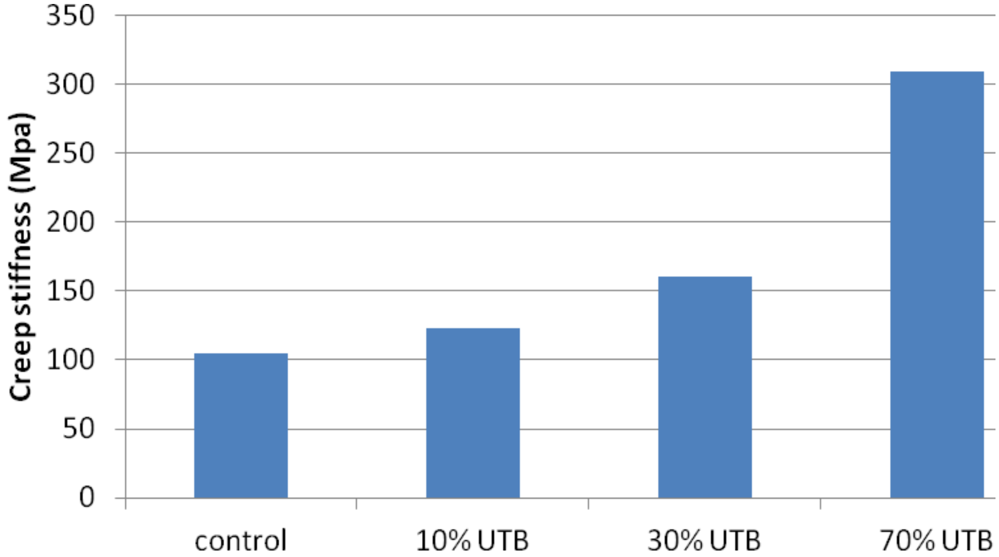


Figure 5-16: Creep stiffness of control binder, 10%, 30% and 70% UTB bioasphalt at 60s during BBR test

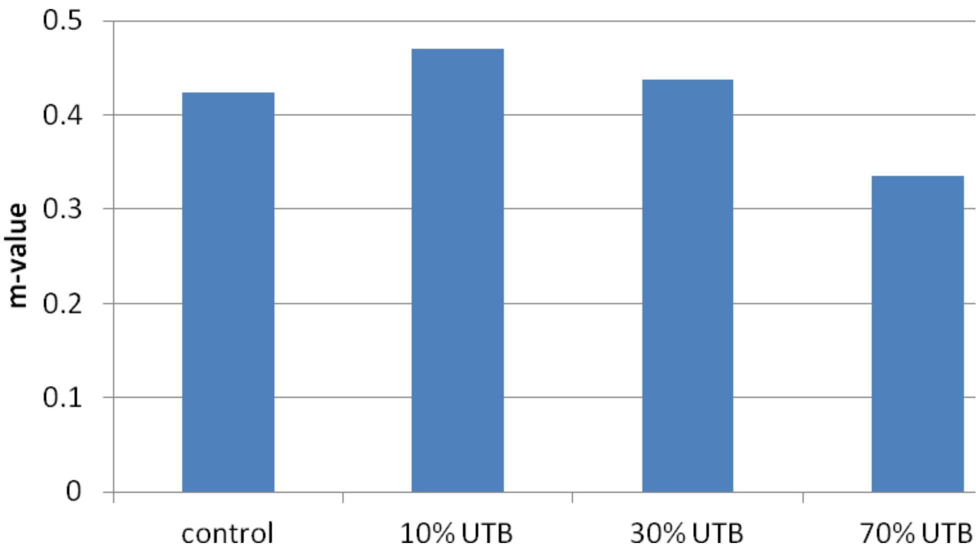


Figure 5-17: M-value of control binder, 10%, 30% and 70% UTB bioasphalt at 60s in BBR test

Figure 5-18 and Figure 5-19 show the BBR test results of control binder, 10%, 30% and 70% TB bioasphalt. With the increase of bio oil percent in the bio asphalt, the creep stiffness increased. Figure 10 shows the creep stiffness and m-value of PG 58-28, 10%, 30% and 70% bio asphalt binders at 60s in the BBR test. The creep stiffness of 10%, 30% and 70% bio oil blended asphalt binders are 34.3%, 74.8% and 101.9% higher than that of the control binder respectively. The m-value of 10%, 30% and 70% bio oil blended asphalt binders at 60s were 3.16%, 4.57% and 6.09% lower than the control binder respectively. This also indicates that the blending of bio oil into the asphalt binders would decrease the low temperature cracking performance.

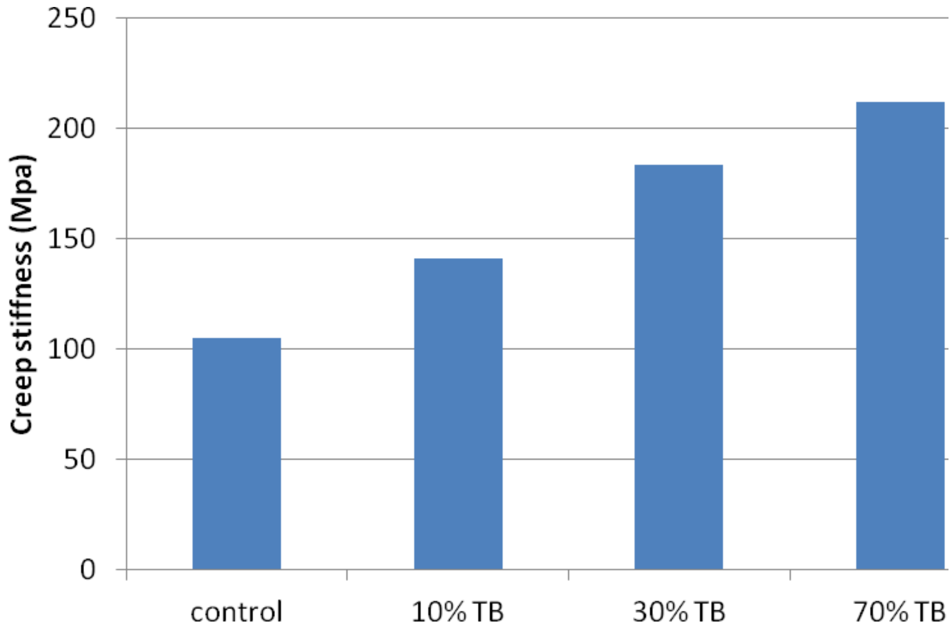


Figure 5-18: Creep stiffness of control binder, 10%, 30% and 70% TB bioasphalt at 60s during BBR test

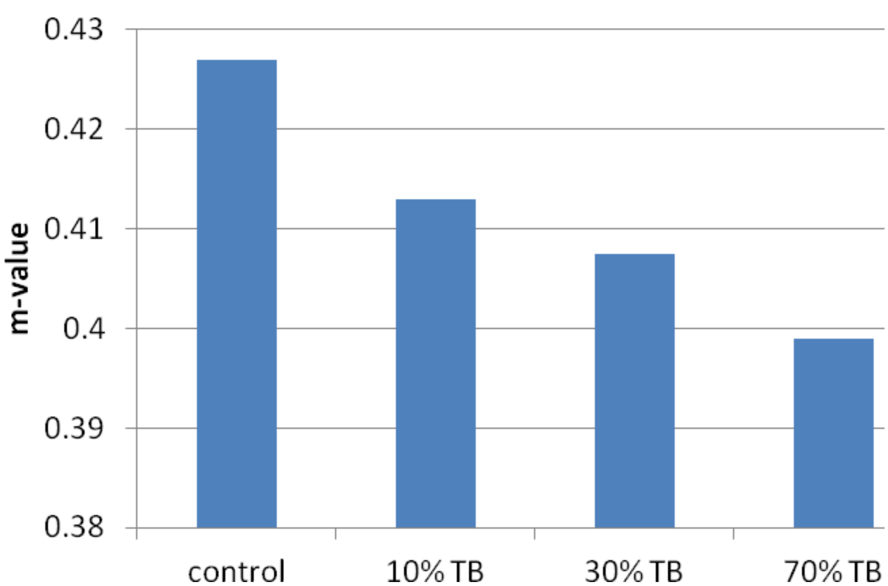


Figure 5-19: M-value of control binder, 10%, 30% and 70% TB bioasphalt at 60s in BBR test

Figure 5-20 and Figure 5-21 show the BBR test results for control binder, 10%, 30% and 70% PMB blended asphalt binders. It is observed that with the increase of the PMB percent in the asphalt binders, the creep stiffness also increased. The creep stiffness of 10%, 30% and 70% PMB blended asphalt binders at 60s were 16.2%, 48.5% and 207.6% higher than that of the control binder. The m-value showed a overall decrease trend with the increase of PMB percent except that the m-value of 10% PMB bioasphalt was slightly higher than that of control binder. The test results indicate that with the increase of PMB percent in the bioasphalt, the low temperature performance would decrease overall.

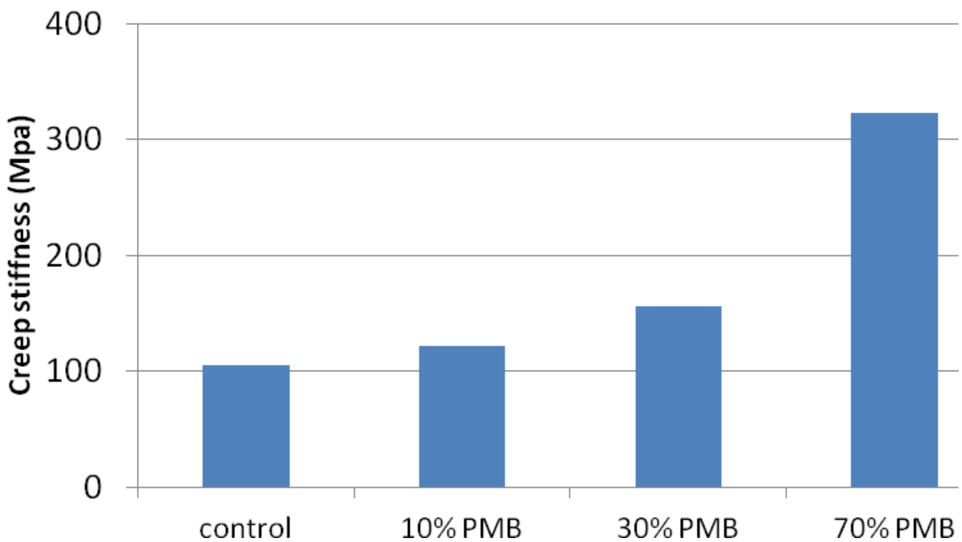


Figure 5-20: Creep stiffness of control binder, 10%, 30% and 70% PMB bioasphalt at 60s during BBR test

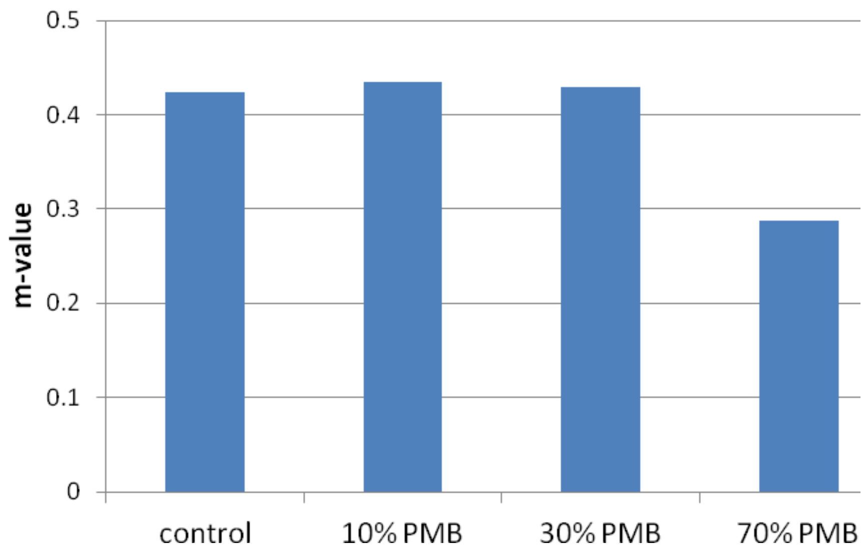


Figure 5-21: M-value of control binder, 10%, 30% and 70% PMB bioasphalt at 60s in BBR test

Figure 5-22 and Figure 5-23 illustrate the comparison results among three different types of bio oil blended asphalt binders. The PMB and UTB bioasphalt showed similar creep stiffness values for different bio oil percentages. The TB bioasphalt was stiffer than PMB and UTB blended asphalt binders at 10% and 30% points but softer at 70% point. The UTB bioasphalt showed the highest m-value at 10% and 30% points, followed by PMB and TB bioasphalt. TB blended asphalt binder showed highest m-value at 70% point, followed by the UTB and PMB bioasphalt. The comparison results indicate that when the bio oil percentage is low, UTB bioasphalt is expected to have the best low temperature performance, followed by PMB and TB bioasphalt. However, when the bio oil percentage is high, TB bioasphalt is expected to have the best low temperature performance, followed by UTB and PMB bioasphalt.

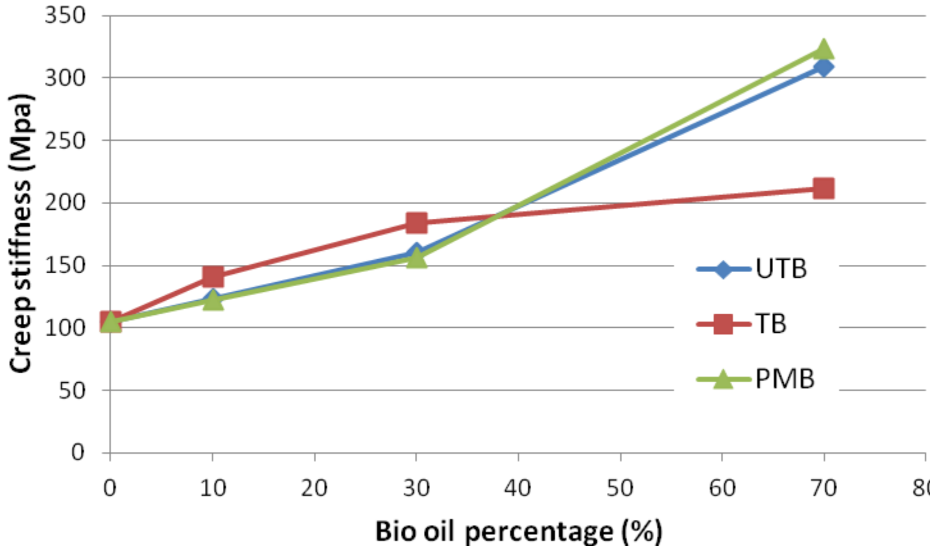


Figure 5-22: Comparison of the creep stiffness of three types of bioasphalt binder at 60s

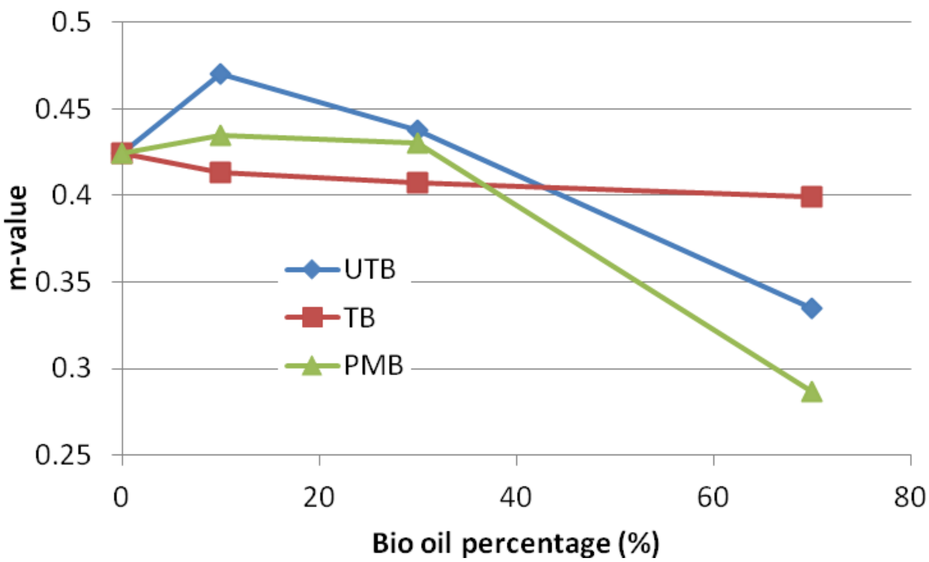


Figure 5-23: Comparison of the m-value of three types of bioasphalt binder at 60s

5.5 Summary of Findings

Theological properties of asphalt binder PG 58-28 and asphalt binders blended with different percentages of bio oils were studied by Superpave^{TM} binder tests. Summaries of findings are presented as below:

1) With the increase of bio oil percentage in the asphalt binder, the rotational viscosities before RTFO aging show decrease trend overall except for the 30% UTB, 30% PMB and

70% PMB bioasphalt, which is possibly due to the over aging of bio oil during mixing or the combination between bio oil and control asphalt binder;

2) After RTFO aging, the rotational viscosity shows a good increase trend with the increase of bio oil percent, but the aging indexes do not present a good increase trend;
3) The DSR test results indicate that with the increase of bio oil percent, a better rutting performance is expected because of the higher complex shear modulus after RTFO aging;
4) The BBR test results indicate that the blending of bio oil into the control asphalt binder would reduce the low temperature performance because of the higher creep stiffness and lower m-value.

CHAPTER 6: MECHANICAL PERFORMANCE EVALUAITON FOR ASPHALT MIXTURES MODIFEID BY BIO OIL

6.1 Introduction

This section of the research addresses the design, laboratory preparation and performance characterization of bio oil modified asphalt mixtures. Essentially, this chapter addresses the challenge of whether bio oil modified asphalt mixtures prepared with typical Michigan aggregate materials can work satisfactorily when used for road pavements in the State.

Five characterization approaches are selected to achieve the principal objective of evaluating the mechanical performance properties of bio-modified asphalt mixtures in relation to its resistance against permanent deformation, moisture susceptibility and fatigue cracking. The characterization methods used are: 1) Permanent deformation or rutting using the Asphalt Pavement Analyzer (APA); 2) Indirect Tensile Strength Ratio (TSR) for moisture susceptibility and; 3) Dynamic modulus for stiffness or E* test; 4) Flow Number (FN) for permanent deformation evaluation; 5) Beam Fatigue Test for fatigue evaluation. Based on the research, recommendations and a guiding framework are made on the proposed use of the three types of bio oil in Michigan asphalt road design and construction.

6.2 Materials

The asphalt binders used in the performance evaluation section includes: control asphalt binder PG 58-28, 5% and 10% UTB, 5% and 10% TB, and 5% and 10% PMB modified asphalt binders. The aggregate used in the study are 1/4 screen and natural sand. The gradation is shown in Table 6-1.

Table 6-1: Aggregate gradation of asphalt mixture used in the study

Sieve No.	1/2”	3/8”	#4	#8	#16	#30	#50	#100	#200
Percent passing (%)	100	99.1	75.0	55.9	41.3	27.5	14.5	7.5	5.5

6.3 Experiment Conduction

6.3.1 Dynamic modulus (E*) stiffness test

Dynamic modulus (E*) test was conducted according to the standard AASHTO TP62-03 specification procedure. The test set up is shown in Figure 6-1 where a cylindrical specimen of 100mm diameter and 150mm height asphalt concrete sample is loaded under the compressive test. The test temperatures are -10°C, 4°C, 21.3°C and 39.2°C, and frequencies of 25Hz, 10 Hz, 5 Hz, 1 Hz, 0.1 Hz and 0.01 Hz.

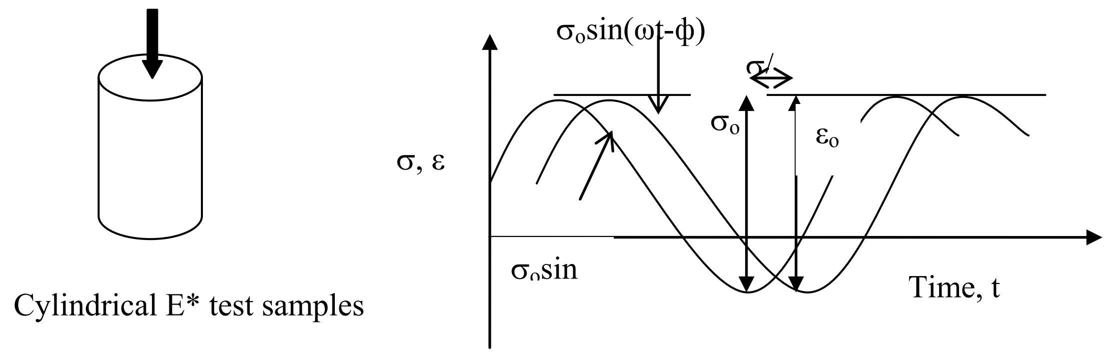


Figure 6-1: Haversine loading pattern for the dynamic modulus test

In calculating the dynamic modulus and phase angle parameters, the applied stress and its resulting recoverable axial strain response of the specimen is measured during the test. The dynamic modulus is then evaluated as the ratio of the amplitude stress (σ) and amplitude of the sinusoidal strain (ε) that results in a steady state response at the same time and frequency as indicated in equation 6-1.

$$E^* = \frac{\sigma_0}{\varepsilon_0} \qquad \textbf{(6-1)}$$

Where:

σ_0 = peak (maximum) stress

ε_0 = peak (maximum) strain;

Figure 6-2 to Figure 6-4 displayed the dynamic modulus master curve for control asphalt mixture and three types of bio oil modified asphalt mixtures. Based on the test results, it is observed that 10% UTB and 5% TB modified asphalt mixtures had higher |E*| than the control asphalt mixture while 5% UTB and 10% TB modified asphalt mixtures had lower |E*| compared to the control asphalt mixture. Both 5% and 10% PMB modified mixture had higher |E*| than the control asphalt mixture. The reason why the |E*| results didn't show the same trend as the |G*| results is thought that the short-term aging of asphalt mixture during the mixing and compaction was not as high as that in the RTFO aging simulation because the mixture was mixed at 147°C, compacted at 135°C, and aged for two hours, while the RTFO test was conducted at 163°C for 85 minutes with abundant fresh air.

The DSR binder test results showed that the UTB and TB have lower complex shear modulus than the control binder before RTFO aging but have higher complex shear modulus than the control binder after RTFO aging. So the complex shear modulus of UTB and TB modified asphalt binder may still be softer than the control binder if the aging level during mixing and compaction was lower than that in the RTFO test. Because the mixing and compaction temperature were 147°C and 138°C respectively, and the aging time was two hours without as much fresh air as the RTFO test, it is possible that the aging of asphalt binders during the mixing and compaction was not as high as that of the RTFO simulation. As a result, the |E*| of bio oil modified asphalt mixtures may also be still lower than the control binder. The polymer in the PMB modified asphalt mixtures contributed to the higher |E*| value compared to the control asphalt mixture.

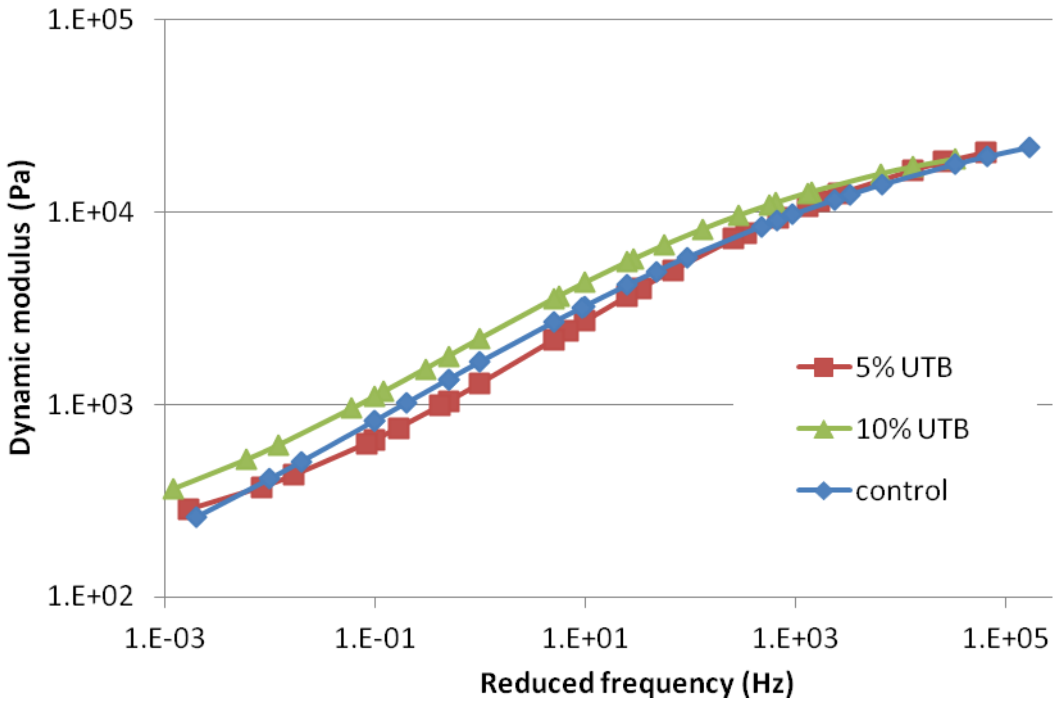


Figure 6-2: Dynamic modulus master curve plot for control asphalt mixture, 5% and 10% UTB modified asphalt mixture

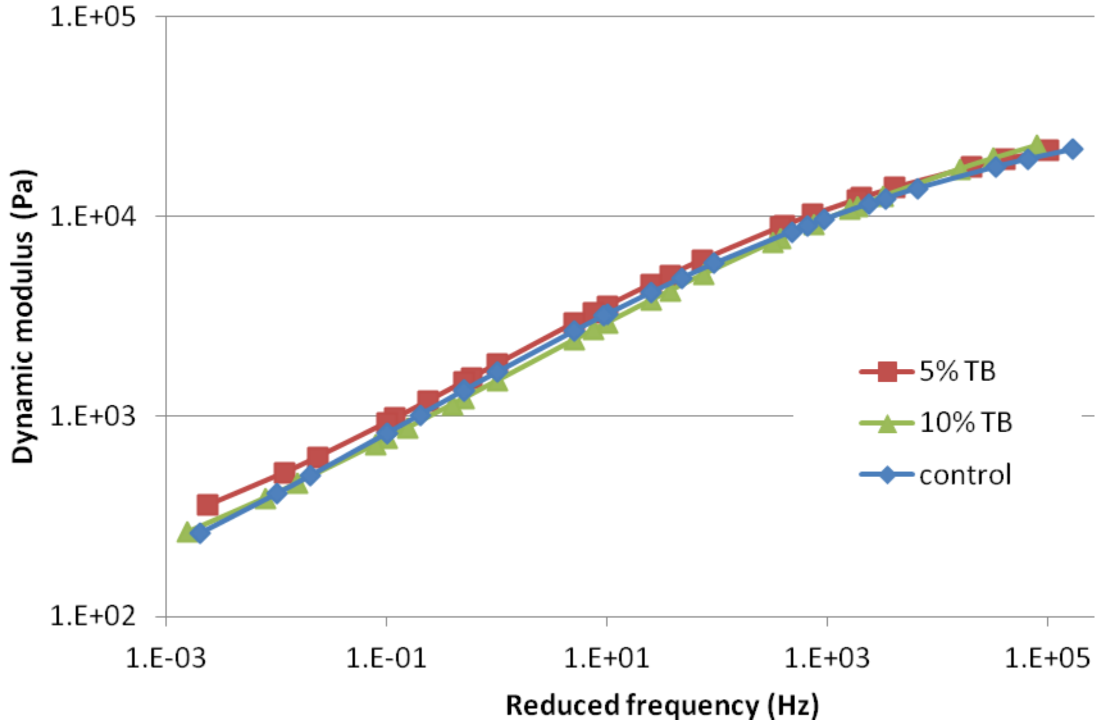


Figure 6-3: Dynamic modulus master curve plot for control asphalt mixture, 5% and 10% TB modified asphalt mixture

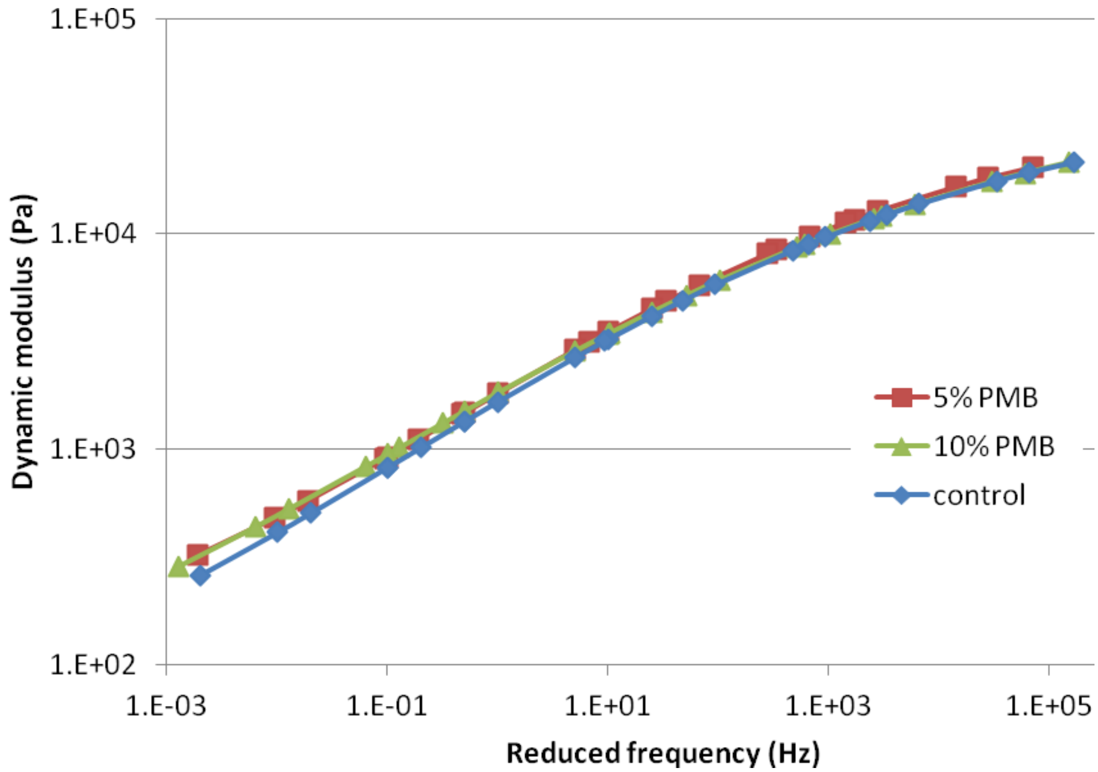


Figure 6-4: Dynamic modulus master curve plot for control asphalt mixture, 5% and 10% PMB modified asphalt mixture

6.3.2 Permanent deformation (rutting) characterization

The National Co-operative Highway Research Program (NCHRP) defines permanent deformation or rutting in asphalt pavements as "*the accumulation of small amounts of unrecoverable strain resulting from applied loads to the pavement*". It further states that this deformation phenomenon is caused by consolidation which is a lateral movement of the HMA under traffic or both. In order to understand effect of using the prepared wood-waste bioasphalt in the PG 58-28 control asphalt binder, the Asphalt Pavement Analyzer (APA) is used. The hose pressure was applied for 8,000 cycles at a temperature of 58°C, which is the maximum anticipated temperature during the field performance of the pavement. The parameter of interest is the rutting depth recorded after the 8,000 cycles of loading. Figure 6-5 shows the APA set up used in this research.

Figure 6-5: Set-up of the Asphalt Pavement Analyzer for rutting performance

Figure 6-6 and Figure 6-7 display the APA test results of control HMA mixture, 5% and 10% UTB modified HMA mixture, 5% and 10% UTB modified HMA mixtures, and 5% and 10% UTB modified HMA mixtures at 58°C.

It is observed most of the bio oil modified asphalt mixtures showed higher rutting depth than the control asphalt mixture. Detailly, for UTB modified HMA mixture, the rutting depth of 10% UTB modified HMA mixture after 8000 cycles of loading was the highest, followed by 5% UTB modified HMA mixture and the control mixture. For both TB and PMB modified HMA mixtures, 5% bio- modified HMA mixture turned out to show the highest rutting depth while the rutting depth of control HMA mixture and 10% bio oil modified HMA mixture showed very close final rutting depth.

As mentioned before, the aging during the mixing and compaction may be lower than that in the RTFO test, which made the bio oil modified asphalt mixture still softer than the control asphalt mixture after mixing and compaction, which resulted in a higher rutting depth in the APA test.

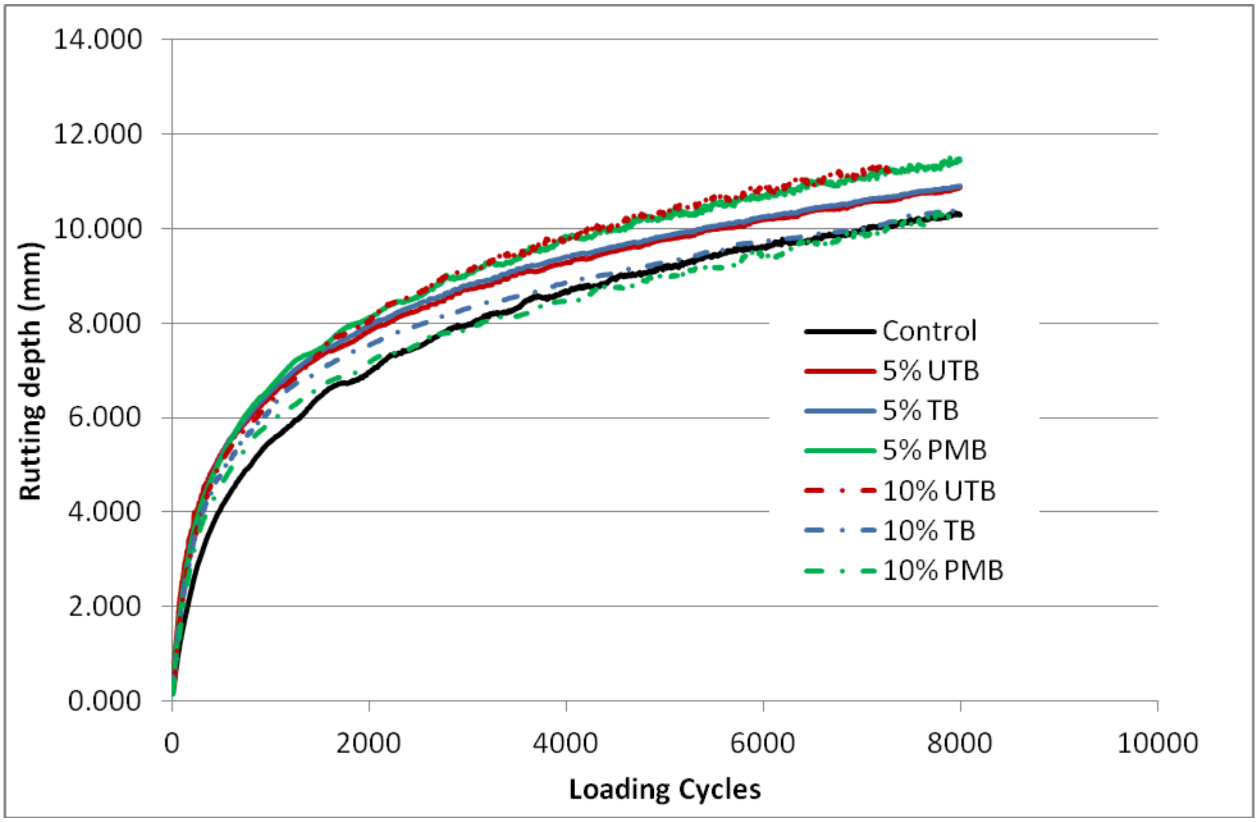


Figure 6-6: The APA test results for control HMA mixture and bio oil modified HMA mixture at 58°C

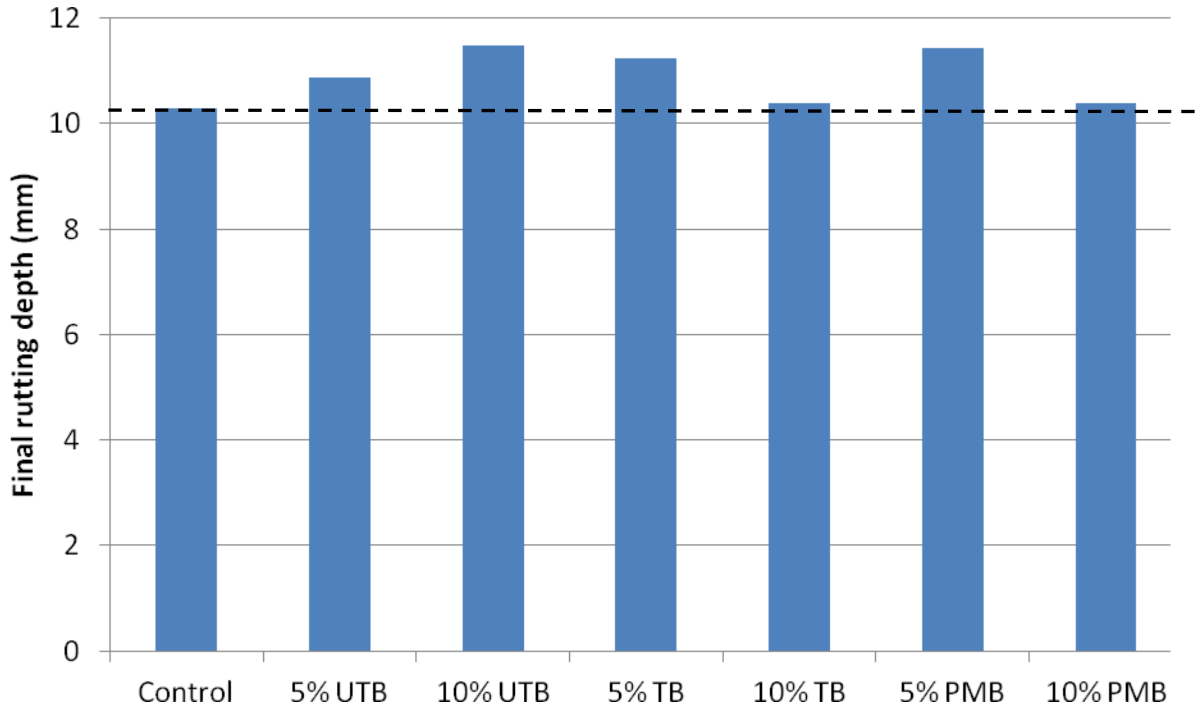


Figure 6-7: The final rutting depth of control HMA mixture and bio oil modified HMA mixtures at 58°C

6.3.3 Moisture susceptibility characterization

One property of asphalt concrete essentially used for evaluating the bioasphalt pavement mixture's susceptibility to moisture damage is the indirect tensile strength at a constant rate of loading (Quintus 1991). The indirect tensile method was used to develop tensile stresses along the diametric axis of the test specimen as specified in the AASHTO T283, "*Resistance of Compacted Bituminous Mixture to Moisture-Induced Damage*," for evaluating an HMA mixture's susceptibility to moisture damage. The laboratory set-up used for this study is shown in Figure 6-8. Based upon the theory of elasticity, the strain is expressed in three dimensions. The loading condition was 0.833mm/sec. and a constant strain rate of until it fails by splitting along the diametric axis. From the results, the horizontal tensile stress and tensile strain at the center of the test specimen is calculated using Equation 6-3 and Equation 6-4, respectively.

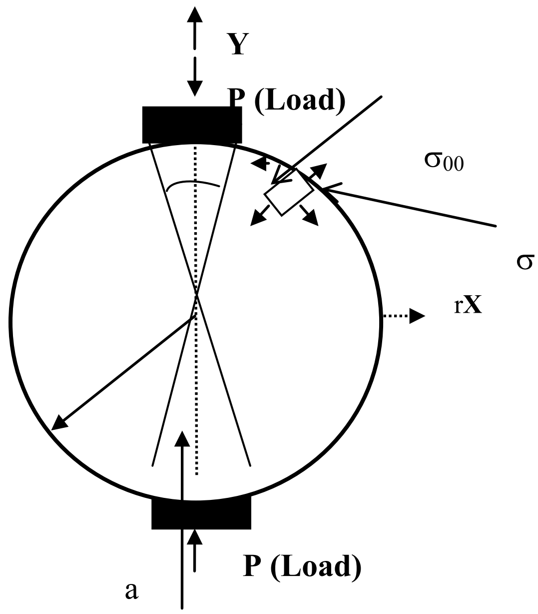


Figure 6-8: Schematic of the indirect tensile strength test for moisture susceptibility

$$\text{Horizontal Tensile Stress} = \sigma_{xy} = \frac{2P}{\pi t d} \tag{6-3}$$

Where:

d = the diameter of the specimen,

P = the applied load, and

t = the thickness of the test specimen or core; and

$$\text{Horizontal Tensile Strain} = \varepsilon_{xx} = \delta_{xx}\left[\frac{2(1+3\mu)}{d(a+b\mu)\pi}\right] \tag{6-4}$$

Where:

ε_{xx} = horizontal deformation across test specimen

μ = Poisson's ratio and;

a, b, d = integration constants that are specimen geometry dependent

Finally, the indirect-tensile strength ratio is calculated below.

$$\text{IDT TSR} = A / B$$

Where A = the indirect-tensile strength (unconditioned) samples, kPa

B = the indirect-tensile strength of dry (unconditioned) samples, kPa

Figure 6-9 shows the IDT test results for dry and conditioned control asphalt mixtures and bio oil modified asphalt mixtures. Based on the test results, it is found that most of the bio oil modified asphalt mixture had lower indirect tensile strength than the control asphalt mixture. It is interesting that all of the tensile strength ratio (TSR) values of the asphalt mixtures were higher than one. The reason for this is thought certain system error occurred during the test but without much effect for the comparison results. The TSR values of control asphalt mixture, the 5% UTB, TB and PMB modified asphalt mixtures were almost the same. The TSR values of 10% UTB, TB and PMB modified asphalt mixtures were lower than the control mixture and 5% bio oil modified asphalt mixtures.

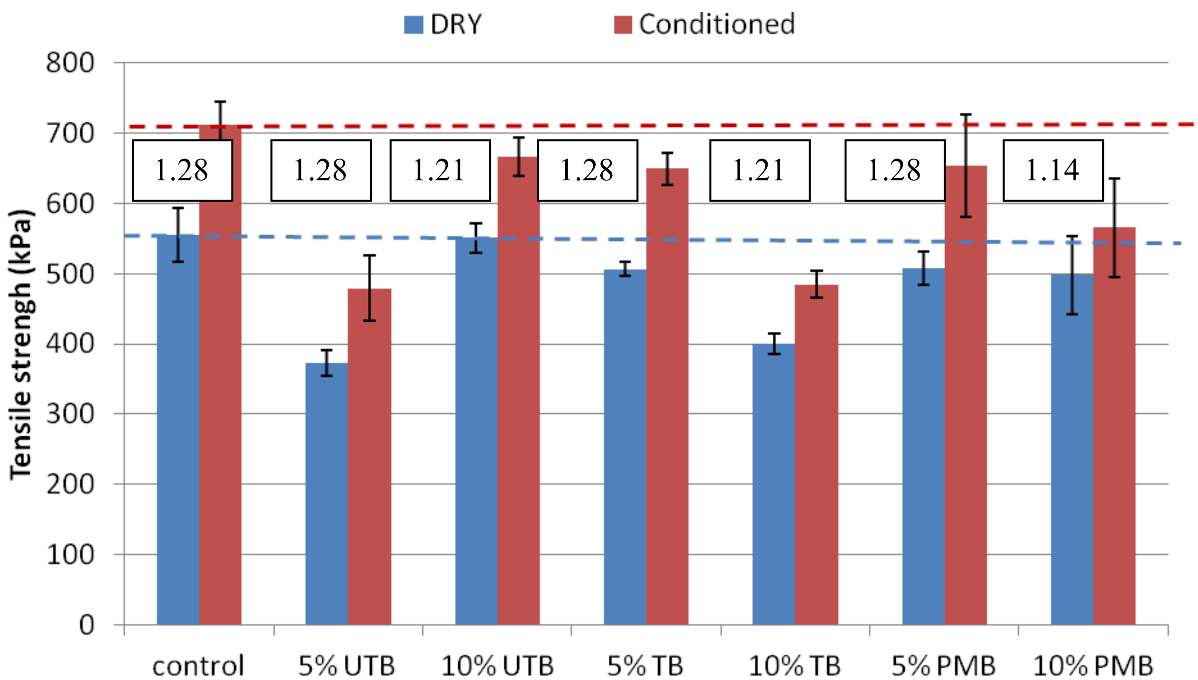


Figure 6-9: Indirect tensile strength results for dry and conditioned asphalt mixtures

6.3.4 Four Point Beam Fatigue Test

Fatigue is the damage occurring in a material due to the application of cyclic loading. The purpose of this test is to determine the fatigue life of the asphalt mixture subjected to the repeated bending until failure where the fatigue failure was defined as 50% reduction of initial stiffness (AASHTO:T321-07 2007). In this test, a maximum of 200 micro-strain at 10Hz is applied on the sample until the flexural modulus is half of the initial modulus for all the samples. Then, another maximum of 400 micro-strain at 10Hz is applied until the flexural modulus is half of the initial modulus. Figure 6-10 shows the set-up for the four point beam fatigue test.

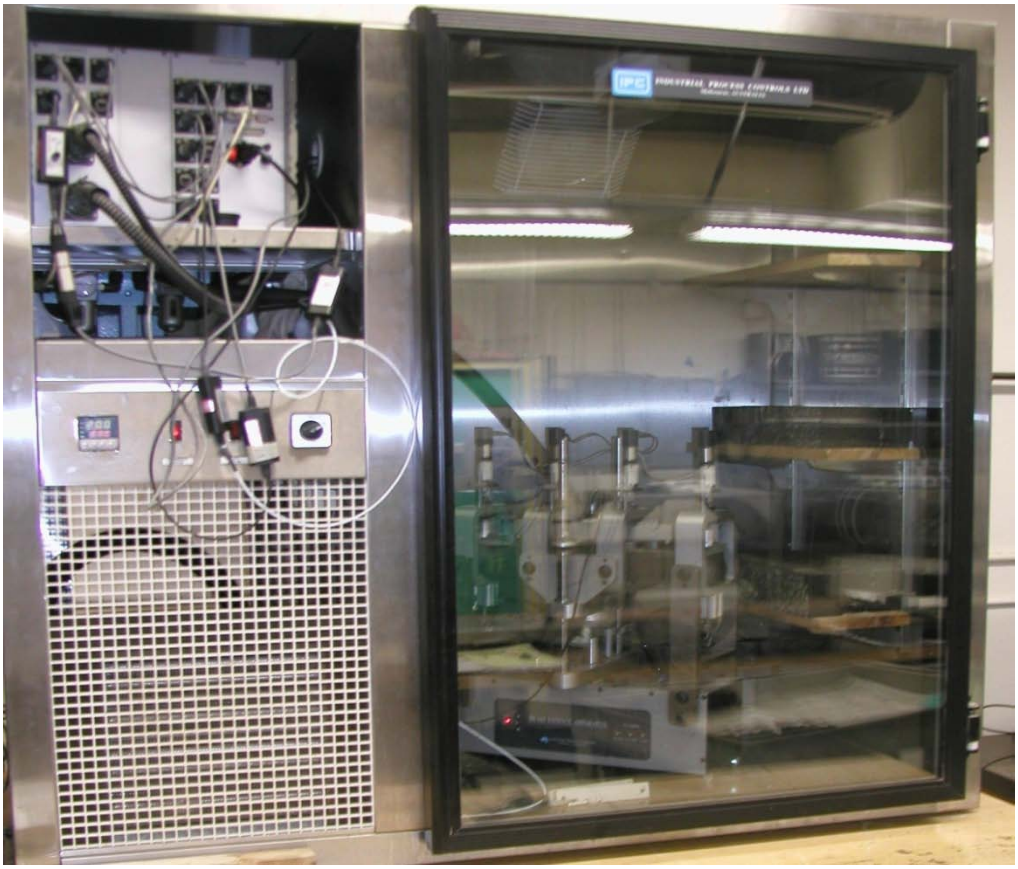


Figure 6-10: The set-up of the four point beam fatigue test

Figure 6-11 shows the four point beam fatigue test results for control asphalt mixture, 5% UTB, 5% TB, 5% PMB, 10% UTB and 10% PMB bioasphalt mixtures under 200 micro strain and 400 micro-strain respectively. It is observed that all of the bio oil modified asphalt mixtures had higher fatigue lives than the control asphalt mixture at both 200 and 400 micro-strains. The test results mean that the bio oil modified asphalt mixtures are expected to obtain better fatigue performances than the control asphalt mixtures. The DSR test results for the PAV aged binder is thought to be an index for the fatigue life. Thus, the beam fatigue test results for asphalt mixtures also show a different trend from the binder test. The possible reason for this is mainly that the aging of asphalt mixture in the four point beam fatigue is much lower than the aging level in the PAV test.

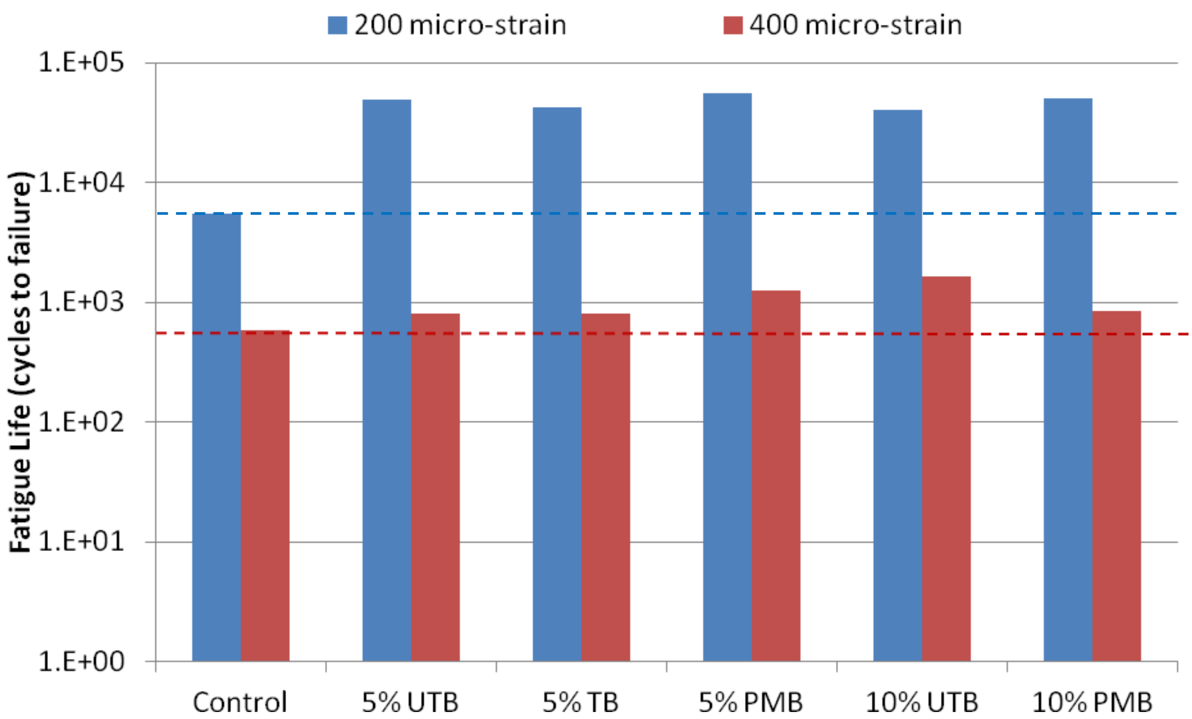


Figure 6-11: Results of four point beam fatigue testing for control asphalt mixture, 5% UTB, 5% TB, 5% PMB, 10% UTB and 10% PMB bioasphalt mixtures

6.4 Conclusions

In this study, the three types of bio oils (UTB, TB and PMB) derived from waste wood resources were added into the petroleum based asphalt binders to evaluate the effect of the bio oils on the asphalt mixture performances. Based on the test results, the following conclusions were made:

1) The addition of bio oil can improve the fatigue performances of asphalt mixtures significantly.
2) Bio oil doesn't negatively affect the moisture susceptibility of asphalt mixtures although there is a slight reduction for the indirect tensile strength.
3) The addition of bio oil has slightly negative effect on the rutting performance of the HMA mixtures.
4) The polymer modified bio oil overall performs better than the untreated bio oil and treated bio oil for the asphalt mixture performances. However, this effect is limited when the bio oil content is low.

In conclusion, bio oils generated from waste wood resources can be a good extender and modifier for the petroleum based asphalt binders when the bio oil fraction is low (not higher than 10% by weight).

CHAPTER 7: LIFE CYCLE ASSESSMENT AND ENVIROMENTAL EFFECT EVALUATION

7.1 Introduction

The availability of abundant forest wood in Michigan makes the development of bioasphalt from bio oils very beneficial to revolutionize the asphalt paving industry in the coming years. Furthermore, it is pertinent that the viability of the relevant phases involved in the utilization of bioasphalt for paving mixtures to be assessed through a preliminary life cycle guiding framework. For Michigan to satisfactorily implement bioasphalt as an asphalt pavement modifying material, the social, economic and environmental impacts need to be established. Due to the absence of raw, first-hand data or information the investigation is conducted in the form of the creation of a basic model life cycle assessment and impact analysis scheme to show the relevant metrics of interest needed. This basic model is complemented by information from past research. Additionally, the various types of impact that Michigan can accrue from implementing the use of bioresources in asphalt pavements is discussed briefly.

The objective of this chapter is to first define and develop a simple LCA guiding framework based on all the critical project phases necessary for pyrolyzing wood waste into bioasphalt, preparing bio oil modified asphalt mixtures and the constructing pavement structures using bio oil modified asphalt mixtures. The impact of utilizing bioasphalt in Michigan paving mixtures is also categorized in terms of geographic extents. Another objective is to evaluate and explain some of the potential merits of using bioasphalt as a partial replacement to petroleum-based asphalt in asphalt pavements.

7.2 Life cycle assessment (LCA) methods

The methods employed in this basic life cycle outline sets out to enlighten asphalt pavement transportation stakeholders in Michigan on the environmental soundness or otherwise of integrating bioasphalt into the design, construction of State roads and highways. The International Organization for Standardization's document, ISO 140-14049, was referenced in undertaking this LCA study. The goal of this LCA is to define the major and minor factors that will impact the life cycle greenhouse emissions based on: 1) the production of the pyrolyzed bio-oil; 2) design, construction of the asphalt pavement. The operational phases outlined to achieve the LCA goal includes wood waste collection/harvesting, wood waste transportation, pyrolysis of wood waste into bioasphalt, bio asphalt transportation, HMA preparation and road paving processes. Furthermore, the system boundaries for this LCA are chemicals, energy, fuels and transportation while the functional unit is considered to be 1 lane mile of bio oil modified asphalt road or highway. In Figure 1, an inventory showing the boundary conditions is provided as a basis for this LCA.

7.2.1 Waste wood collection/harvesting

In this LCA analysis framework, the feedstock is wood chips, sawdust and shavings collected from sawmills and also logging residue collected after harvested timber on forest lands. The key inputs are fuel for transporting the wood waste to the bioasphalt plant and for grinding the feedstock. To eliminate the greenhouse gas environmental impact of the wood waste harvesting, it is proposed that the bioasphalt plants in Michigan be located close to forest (timber) land or sawmills to reduce the transportation distance or produce the bioasphalt on site.

Wood waste transportation

In situations where the bioasphalt plants are designed and located away from the saw mills or logging sites, a mathematical model needs to be used to determine the transportation distance between the collection points and the bioasphalt plants. Equation 7-1 was proposed by Williams and Boateng and they used it to model the distance between typical biomass collection sites and pyrolysis plants (Wright et al. 2008). This same equation can be adopted for use in estimating the radial distance between the wood waste collection sites and the bioasphalt plant

$$\bar{r}_{circle} = \frac{2}{3}\tau\sqrt{\frac{F}{\pi Y f}} \qquad \textbf{(7-1)}$$

Where:

τ = road tortuosity factor (1.5 as obtained from literature)

F = biomass (wood waste) required to generate the required amount of bioasphalt

Y = biomass (waste wood) yield in short tons/acre

f =fraction of the land devoted to biomass crops (0.10 as obtained from literature)

In calculating the mass of wood waste required to produce the bioasphalt in Michigan, F, Williams and Boateng have proved that it is related to the energy contents of gasoline (EG) and biomass (EB, assumed to be 19.5 MJ/kg), the biomass to liquid (BTL) fuel efficiency, ηBTF, and the plant capacity, M, by F = M (EG/ηBTF) EB. Furthermore, it must be stated that the M is expressed in gallons of gasoline equivalent (gge)/year units which is alternatively expressed as energy units by a factor of 31.8 MJ per gallon of gasoline. Since this Michigan bioasphalt was developed via the fast pyrolysis process, researchers have proved that for a fast pyrolsysis system, the BTL fuel efficiency, ηBTF, is approximately 40%. Fan et al. had used an F value of 400 tonnes bone dry biomasses/day and the same can be used for this scenario (Fan et al. 2011). Equation 7-1 thus reduces to Equation 7-2. Again, if Michigan developed bioasphalt plants whereby the waste wood is produced on site, the component feedstock transportation can be eliminated and rcircle will be 0.

$$\bar{r}_{circle} = 35\sqrt{\frac{1}{Y}} \tag{7-2}$$

7.2.2 Pyrolysis of wood waste into bioasphalt

In order to put the inputs and outputs for this stage into perspective, it is pertinent to describe briefly the fast pyrolysis process. The estimated 2000lbs of wood chips, sawdust and chippings was first introduced into a shredder and dried in a fluidized bed which used gas running through it. The waste wood was then fed into the pyrolyzer and subjected to hot sand for the reaction to commence under nitrogen gas. The final product was condensed and stored as bio-oil, termed as bioasphalt in this investigation. For the pyrolysis process, the inputs for LCA analysis includes the electricity (energy) required for the both drying of the waste wood materials and bioasphalt production. The bio-char and bio-gas by-products generated are re-looped into the pyrolysis set up as combustible materials for another preheating cycle. Thus, the bioasphalt was considered as the only output. The bio-char and bio-gas can also be utilized.

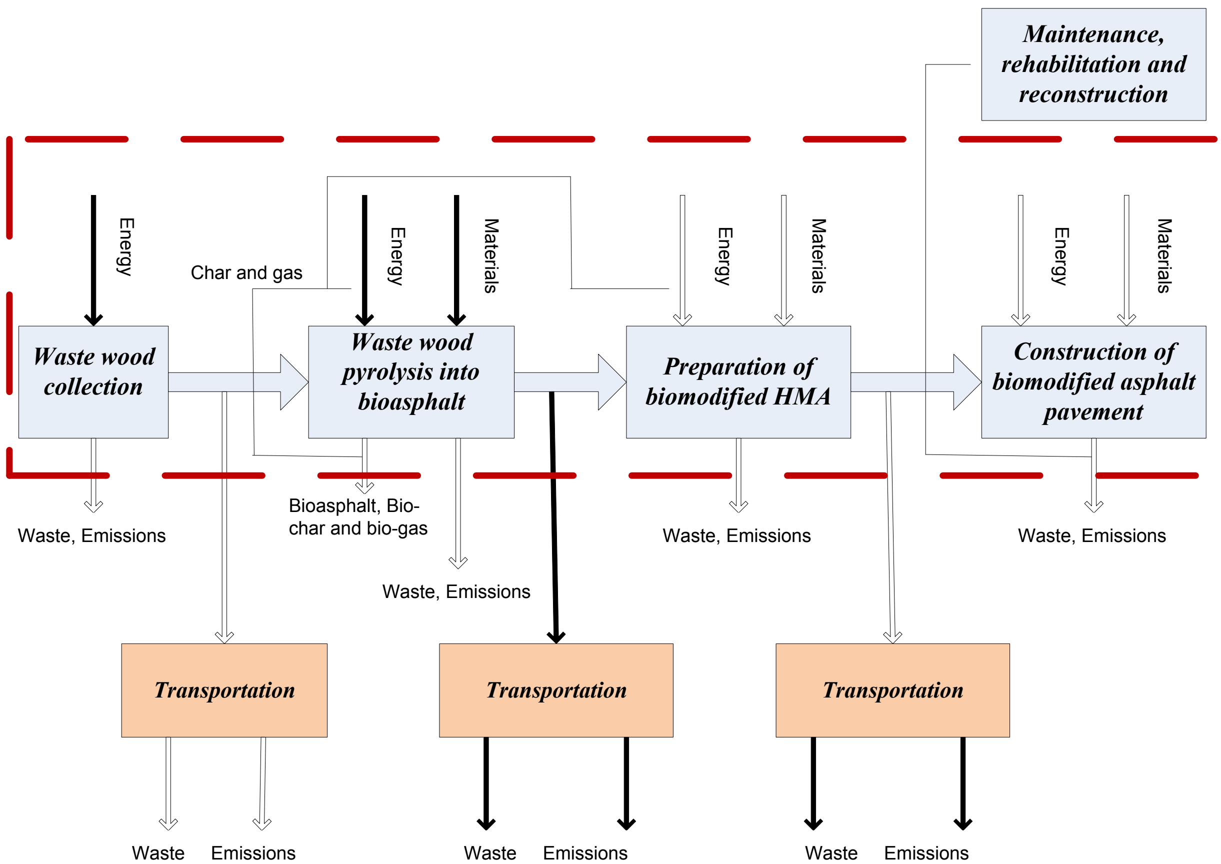


Figure 7-1: Inventory for the bioasphalt production and construction of bio oil modified asphalt pavements

Some researchers evaluated the LCA of electricity generation using fast pyrolysis bio-oil and revealed that the inventory inputs for the process stage as shown in Table 7-1 (Williams and Whitten 1983).

Table 7-1: Fast-pyrolysis Bioasphalt Production (adopted from (Williams and Whitten 1983)

Products		
Pyrolysis bio-oil	1	MJ
Materials		
Waste wood blend	0.08	kg
Water, completely softened	7.2	kg
Processes		
Electricity for wood preheating	0.01	kWh
Electricity for bioasphalt production	0.01	kWh
Natural gas, burned in industrial furnace, low-NO_x	4.5×10^{-5}	MJ
Bioasphalt char combustion emission	1	MJ

7.2.3 Bioasphalt transportation

The bioasphalt produced from the processing plant when transported to available HMA plants in Michigan will require energy from transportation fuel (materials and energy). Before the bioasphalt will be transported, it must be emphasized that this current research experience reveals that the bioasphalt will undergo higher oxidative hardening or aging when exposed to surrounding air. When the developed bioasphalt is stored in silos or storage spaces with sufficient available air above the bioasphalt, it will typically harden or have relatively higher viscosity than petroleum-based asphalt. Therefore, some amount of energy will be required to liquefy bioasphalt before pumping into loading oil tankers. This energy input will add to the energy (fuel) required by the loading oil tankers.

7.2.4 Preparation of bio oil modified HMA

After the bioasphalt is transported to the typical Hot Mix Asphalt (HMA) plant, it will undergo pumping and mixing at elevated temperatures. The HMA mixing plants are located at different contractor facility sites across the State of Michigan. The bioasphalt whether incorporated in the

HMA at 2, 5 and 10% as stated in this research will still require about the same quantity of energy for mixing as if it were typical petroleum-based asphalt. This is based on the earlier knowledge that the bioasphalt had already been liquefied. Even though, the typical mixing temperature of petroleum-based asphalt is about 165 °C, a new temperature specification needs to be set for bio oil modified asphalt which will be characteristically lower than this 165 °C to prevent undue aging, and thereby lowering the energy input. Other inputs for preparing the bio oil modified HMA include fine and coarse aggregates, and any other performance-enhancing modifier.

7.2.5 Construction of bio oil modified asphalt pavements

In this LCA analysis, the construction of the bio oil modified asphalt pavement will involve thelaying and compaction of the HMA over the functional unit of about 1 lane mile. Before these processes, the prepared bio oil modified mixes will be transported in long loading trucks to the project site. Obviously, some energy inputs will be required for the distance and number of truck trips involved here. The HMA upon arriving at the project site, the asphalt mixture will be laid on the roadway and compacted at approximately 135 °C. The energy requirement for the compaction will be expected to be comparatively higher than for 100% pure unmodified PG 58-28 HMA due to the observed influence of RTFO and PAV aging. It is hypothesized that if bioasphalt can be employed as Warm Mix Asphalt (WMA) in the future instead of the conventional HMA, energy input savings of the order 30% can be realized here. Typically, from past research investigations, WMA has compaction temperature range of 250°F (121°C) to 275°F (135°C) while the HMA has a range of 280°F (138°C) and 320°F (160°C) (Harrison and Christodulaki 2000). A detailed flowchart of the identifiable processes for the bio oil modified asphalt pavement construction is given in Figure 2. The flow chart, adopted from LCA research investigations by Huang et al. (Huang et al. 2009), is an expansion of the preparation of bio oil modified HMA and construction of bio oil modified asphalt pavements sections of Figure 7-1.

7.2.6 Maintenance and rehabilitation of bio oil modified pavements

The maintenance and rehabilitation of bio oil modified asphalt pavements is not considered in this basic LCA investigation. It is therefore outside the scope and placed outside the boundary conditions set up as shown in Figure 7-1.

7.3 Potential GHG emissions

7.3.1 Waste wood collection/harvesting

Due to lack of available first-hand data in conducting the greenhouse gas (GHG) emissions from collecting the waste wood, information and data from a similar project as done by Fan et al. is referenced and used (Fan et al. 2011). Fan et al. had stated that in favoring logging reside compared to cultivated systems, the use of fertilizers and pesticides will not be needed but conversely, using biomass from cultivated forest lands for bio oils also yields higher outputs. Fan et al. have proved that the GHG footprint to produce a 1 kg logging residue is 27.4g CO_2 eq./kg. It must be emphasized that if waste wood, chips and shavings is obtained from saw mills with the bioasphalt plant stationed very close or on same site as sawmills, no material inputs or energy is required and therefore no GHG is anticipated ed for the waste collection/harvesting stage.

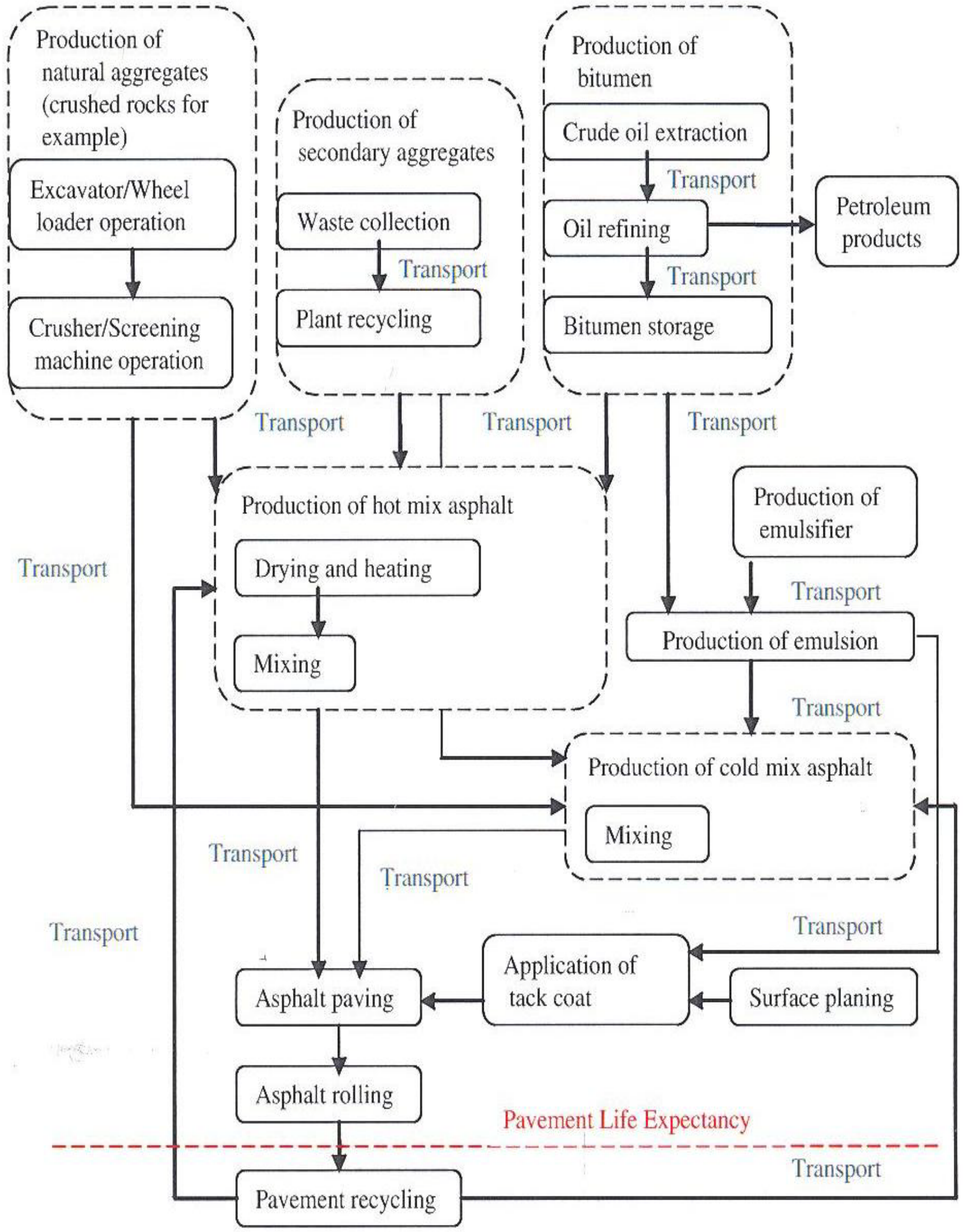


Figure 7-2: Typical unit processes in asphalt pavement construction works

7.3.2 Bioasphalt production

With the bioasphalt plant used for this project, if the facility has available 400 tonnes waste wood/day as feed stock, it will be capable of producing an estimated 8.0 tons of bioasphalt. This is due to the fact that the facility has a yield rate of 1kg (0.001 ton) bioasphalt from the combined Michigan wood mass of 50 kg (0.06 tons). Fan et al. reported that the GHG emission for producing bio-oil (bioasphalt) from logging residue is 14.51g CO_2 eq./MJ and from waste wood, the value is 8.59g CO_2 eq./MJ (Fan et al. 2011).

Preparation of Bio oil modified HMA

Based on a review of current LCIA methods and research works of both the United Kingdom Building Research Establishment (BRE) and ISO14047, the 11 major environmental impact categories for asphalt pavement construction are shown in Table 7-2.

Table 7-2: Environmental impact categories of asphalt pavement construction

Classification and Characterization (selected)				
Impact category	**Inventory loading**	**Unit of characterization**	**Value of characterization factor**	**Source**
Depletion of minerals	Aggregates	tonne minerals	1	BRE
	Asphalt		1	
Depletion of fossil fuels	Energy (MJ)	MJ	1	
Global Warming	CO_2	kg CO_2-eq. (100 years)	1	IPCC
	CH_4		23	
	N_2O		296	
Stratospheric ozone depletion		kg CFC-eq.		WMO
Acidification	SO_2	kg CO_2-eq.	1	IISA
	NO_x		0.7	
	NH_3		1.88	
Photo oxidant (ground-level ozone, of fog)	SO_2	kg C2H4-eq.	0.048	CML
	NO_x		0.028	
	NH_3		0.027	
	CH_4		0.006	
	NMVOC		1	
Human toxicity: emission to air	SO_2	kg, 1, 4-dichlorobenzene-eq.	0.096	CML
	NO_x		1.2	
	CO2		2.4	
	HC		5.70E+05	
	NMVOC		0.64	

	PM		0.82	
	NH_3		0.1	
	Heavy metals		5.10E+05	
Human toxicity: emission to fresh H_2O	HC		2.80E+05	CML
	Heavy metals		950.6 (As)	
			22.9 (Cd)	
			12.3 (Pb)	
			1426.0 (Hg)	
Eco-toxicity: emission to air	NMVOC	kg, 1, 4-dichlorobenzene-eq.	3.20E-11	CML
	HC		1480	
	Heavy metals		7.8E+04 (As)	
			3.7E+05 (Cd)	
			2.4E+03 (Pb)	
			410000 (hg)	
Eco-toxicity: emission to fresh water	HC		1.10E+04	
	Heavy metals		4.0E+04 (As)	
			7.4E+04 (Cd)	
			3.7E+02 (Pb)	
			7.2E+04 (Hg)	
Eutrophication	NO_x	kg PO4-eq.	0.13	CML
	NH_3		0.35	
	COD		0.022	
	Phosphate		1	
	Nitrate		0.1	
Noise	Noise/1000 vehicle	DALY		
Depletion of landfill space	Solid waste	m^3 landfill space	1.3 (2.3) E-03	SAEFL

7.4 Discussion of Environmental and Socio-economic Impact

The environmental and socio-economic impact of implementing bioasphaltas an alternative to petroleum-based asphalt binder in Michigan paving mixtures is categorized under local, regional or global impact which is in agreement with work done by Manyele et al. (Manyele 2007). Table 7-3 shows this categorization. Manyele et al. had outlined stress categories and their singular or multiple impacts identified as Human health (H) and Ecological health (E). In graphical form, the environmental impact categories for the bioasphalt pavement construction are shown in Figure 7-3, according to the work done by Huang et al. (Huang et al. 2009). Furthermore, their research proceeded further to distinguish between the areas impacted as Local or town (L), Regional (R), and Global (G). In terms of socio-economic impact, a summary of the local, regional or global geographic scale of impact is given in Table 7-4.

Table 7-3: A summary of the major impact environmental impact and geographic extent; analysis based on reviewed literature - (Manyele 2007)

Stressor Category	Stressors	Major impact category and area impacted
Toxicants	SO_2, SO_3, H_2S	H, E, L, R, G
Particulates	Wood dust, Sand, dust, and ash	H, E, L
Air pollutants	CO, NO_x, CH, NH_3	H, E, L
Solid waste	Char, sand and ash, accidents	H, E, L, R
Physical trauma	Accidents	H, E, L
	Noise	H, E, L
	Odor	H, E, L
Climate change	CO_2, CH_4, Nitrates, Sulfates	E, G
Acidification	NO_2 (HNO_3), CO_2 (HCO_3)	E, R, G
Resource depletion	Water use	E, R
	Ground water pollution	E, L, R
	Topsoil erosion	E, L

Table 7-4: Scale of socio-economic impact of bioasphalt development in Michigan

Socio-economic Category	Specific impact	Major area impacted
Economic	Job creation, tax benefits, regional growth	L, R
Social	Positive behavioral change	L, R
Educational	Research and development	L, R, G

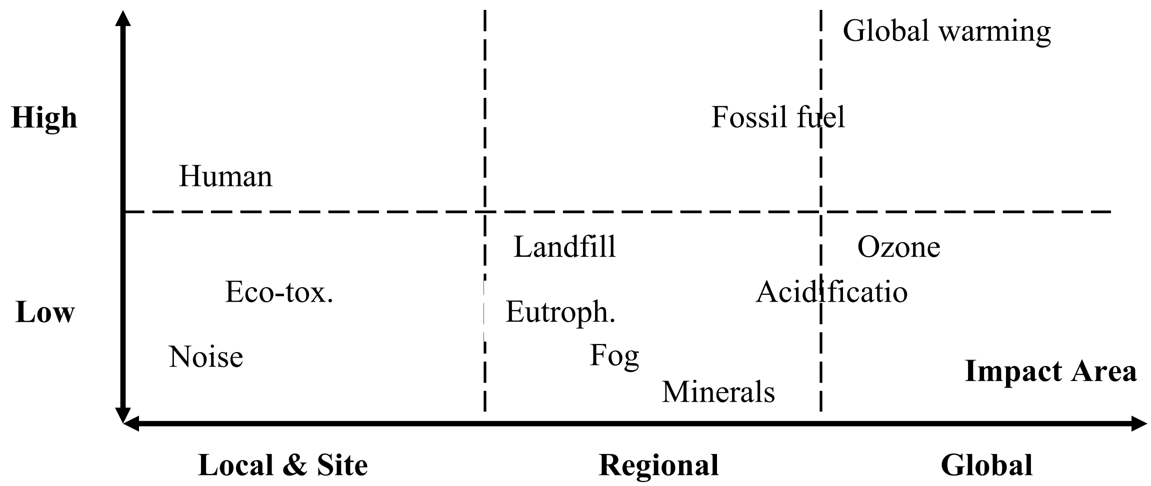


Figure 7-3: Grouping and weighting of environmental impacts categories (adopted from (Huang et al. 2009))

7.4.1 Environmental and Health Impact

Overall, it is anticipated that if CO, CO_2, and PM emissions are considerably lower for bio fuels than for diesel oil as established by Agarwal (Agarwal 1998), then bioasphalt CO, CO_2 and PM emissions will similarly be lower than petroleum-based asphalt use in HMA. It is has been established by research that bio fuel CO, CO_2, and PM emissions are lower than those of dieseloil. The acidity of this Michigan bioasphalt could cause irritation to the human skin and eyes and it was observed during the research that it also had a pungent sharp smell similar to a sulphur-based gas compound. During the mixing of bioasphalt mixture and the RTFO aging for bioasphalt, sharp smell that irritated the eyes were experienced. These are characteristics that could cause health problems to pavement engineers and field workers; however, due to lack of evident data from field paving works, the extent of impact is not measured at this stage.

7.4.2 Job Creation and Regional Growth

The development and implementation of bioasphalt industries in Michigan can be undertaken in tow proposed ways. Firstly, existing bio fuel plants can incorporate bioasphalt development into their current operations to avoid the situation whereby entirely new bioasphalt industries will not need to be created. Secondly, another dimension, is for interested investors and private firms to establish bioasphalt plants as a business venture. Currently, it has been shown as indicated in Figure 4 that Ag Solutions, Inc., Michigan Biodiesel, LLC, Liberty Renewable Fuels, LLC, BioDiesel Industries LLC, NextDiesel LLC, Michigan Biofuels LLC, Milan Biodiesel LLC and

Custom AgriSystems LLC are industries involved in bio diesel production or potential startup in Michigan. It will come as no surprise if any of these believe in the viability of bioasphalt use in HMA and begin to explore it in the future if conclusive research is finalized in this area. Bioasphalt development in Michigan will create more jobs and increase local and state-wide economic growth. From the collection, transportation, conversion and utilization into typical Michigan paving mixtures, new jobs and economic growth will be realized. As many other States are striving to use bio-resources as asphalt replacement alternatives, the export of bioasphalt products across Michigan's borders will expand the regional economy and contribute to national growth.

It has been proved that when bioresources as used for crude-oil, there will be a marked influence on the crude oil market but no influence on the global agricultural markets(Banse et al. 2008). Similarly, since wood-waste bioasphalt will replace portions of crude-oil based asphalt binder, it will translate into crude oil market changes but no significant effect on worldwide food market trends.

Due to the fact that the bioasphalt was processed from waste wood chips, shavings and sawdust of Michigan Aspen, Basswood, Red Maple, Balsam, Maple, Pine, Beech and Magnolia, its development in the State will not be a competing industry with food source plants and vegetations. This is will be beneficial in sustaining the food security ambitions of agricultural stakeholders in the State. Therefore, bioasphalt development will have no negative impact on food security. In providing jobs for Michigan residents, the development of bioasphalt will ensure that rural populations will have improved livelihoods or standards of living since good number of the labor force will come from surrounding communities and cities.

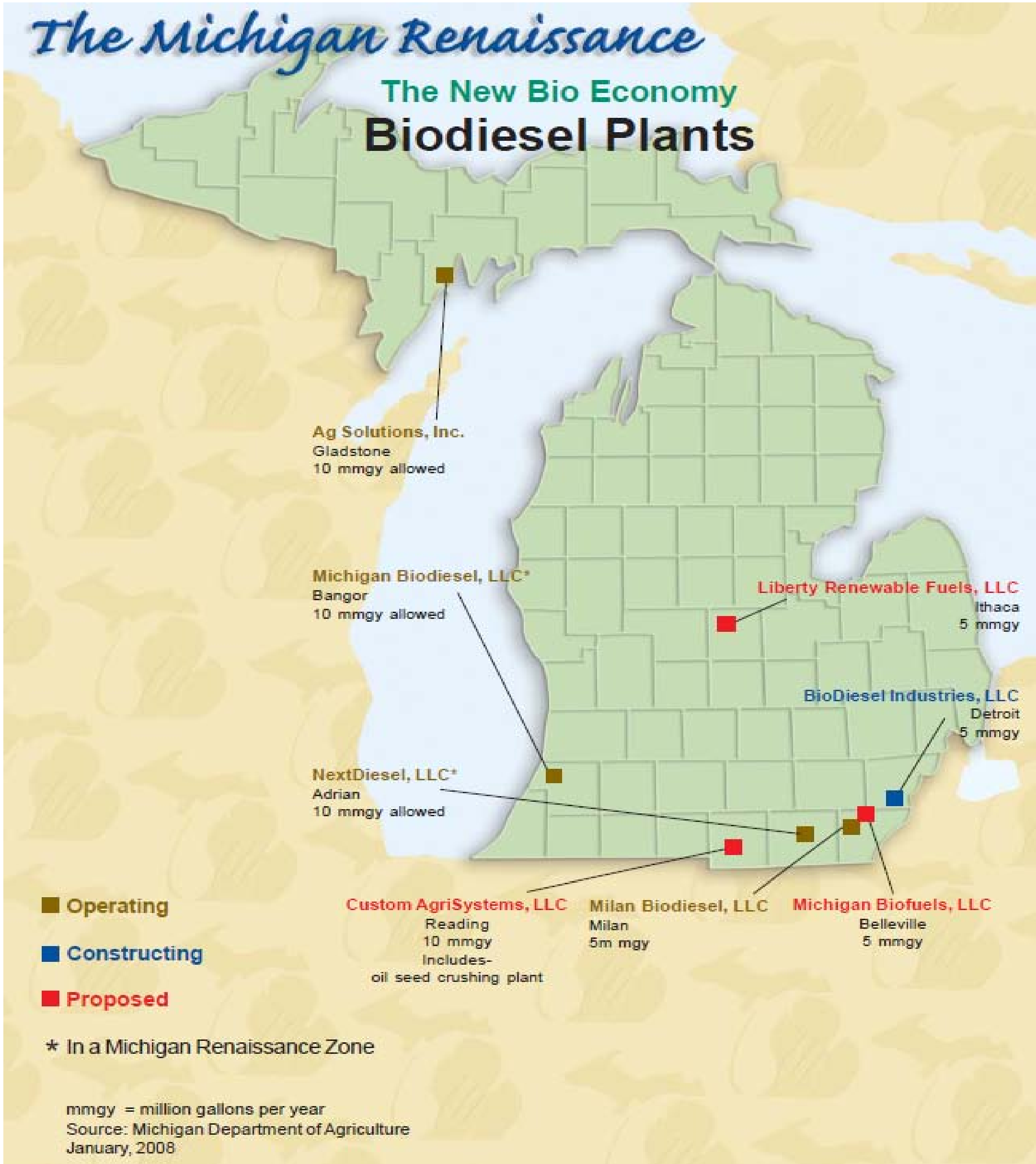


Figure 7-4: A geographical distribution of existing bio fuel processing plants in Michigan Social viability

7.5 Summary and Conclusions

In this section, the life cycle assessment and environmental and socio-economic impact of bioasphalt implementation were discussed. The life cycle assessment included the waste wood collection/harvesting, bio oil process, bioasphalt transportation and bioasphalt maintenance and rehabilitation. The results showed that: 1) it is anticipated that bioasphalt CO, CO_2 and PM emissions are lower than petroleum-based asphalt use in HMA; 2) the acidity of this Michigan bioasphalt could cause irritation to the human skin and eyes; 3) the sharp smell during the mixing, compaction as well as short-term aging can cause significant irritation for eyes; 4) the development of bioasphalt industry is expected to help promote the job creation and regional growth for Michigan.

CHAPTER 8: SUMMARY AND RECOMMENDATIONS

8.1 Summary and Conclusion

This study discussed the implementation of bio oil as a sustainable transportation material. Four main parts were investigated in the study, including: 1) literature review to understand the source collection, producing process, chemical components and some chemical and physical properties of bio oil; 2) compatibility analysis between bio oil and petroleum based asphalt binder; 3) rheological property characterization of asphalt binders modified and partially replaced by bio oil; 4) mechanical performance evaluation of asphalt mixture modified by bio oil; and 5) life cycle assessment and environmental impact of bioasphalt implementation in the paving engineering. Based on the compatibility analysis, it is found that: 1) treated bio oil (TB) which has limited water content can be a good modifier for the petroleum based asphalt binder with good compatibility; 2) with the addition of higher rates of treated bioasphalts in petroleum-based asphalts, conglomeration or assemblage of the asphaltenes will be reached with possible undesirable stiffening effects or loss of some elastic characteristics of the asphalt binder. The asphalt binder test results showed that: 1) virgin bio oil is overall softer than the petroleum-based asphalt PG 58-28; 2) bio oil ages much faster than the control asphalt binder PG 58-28; 3) the addition of bio oil into the control asphalt binder would increase the rutting performance while reduce the fatigue and thermal cracking performance. Based on the mixture performance test, it is found that: 1) the dynamic modulus ($|E^*|$) of some of the bio oil modified asphalt mixture were lower than the control asphalt mixture; 2) the rutting depth of most of the bio oil modified asphalt mixtures were slightly higher than the control mixture; 3) most of the bio oil modified asphalt mixture had higher fatigue lives than the control mixture; 4) the control asphalt mixture and 5% bio oil modified asphalt mixture had higher TSR value than the 10% bio oil modified asphalt mixture; 5) the aging during the mixing and compaction in this study may be still not as high as that in the RTFO aging simulation. The life cycle assessment and environmental impact discussion results showed that: 1) the implementation of bioasphalt can reduce the emission; 2) the aging during the mixing and compaction can cause irritation on the eyes and the skins.

8.2 Recommendations for Bioasphalt Use

8.2.1 Mixing of Bio Oil based asphalt

Bioasphalt is a mixture production consisting of bio oil and petroleum-based asphalt. The first step to produce bioasphalt is to mix the bio oil and the petroleum-based asphalt binder. As previously mentioned, bio oil is very sensitive for temperatures higher than 120°C, so the mixing temperature of bio oil and base asphalt should be not higher than 120°C. In fact, in the experience of the research team, all the three types of bio oils (UTB, TB, PMB) have enough fluidity for the mixing at temperature less than 100°C for the research team took out the bio oil from the plastic bottle by water bath. In the lab mixing, the bio oil and base asphalt were mixed at 110°C by high shear mixer. However, because the bio oil is softer than the base asphalt, the bio oil can obtain equal viscosity at a relatively lower temperature compared to the base asphalt. Thus, in the practical mixing, it is recommended that the mixing temperature for bio oil and base asphalt are different. From the RV test results for control asphalt binder PG 58-28 and pure bio oil in Chapter 5, it is found that the viscosity of pure bio oil at 100°C is close to that of pure PG 58-28 at 120°C. Thus, it is recommended that the mixing temperatures for bio oil and PG 58-28 are 100°C and 120°C respectively.

8.2.2 HMA mixing and compaction

After the mixing of the bio oil and base asphalt, the bioasphalt needs to be heated to the temperature for HMA mixing, as shown in Figure 8-1. After the mixing, the HMA mixture needs to be aged for a certain time. If the bio oil percentage is low (less than 10%), the mixing, aging and compaction can follow the normal procedure. However, if the bio oil percentage is high (more than 10%), it is recommended to reduce the aging time before compaction so that the bioasphalt would not be over aged.

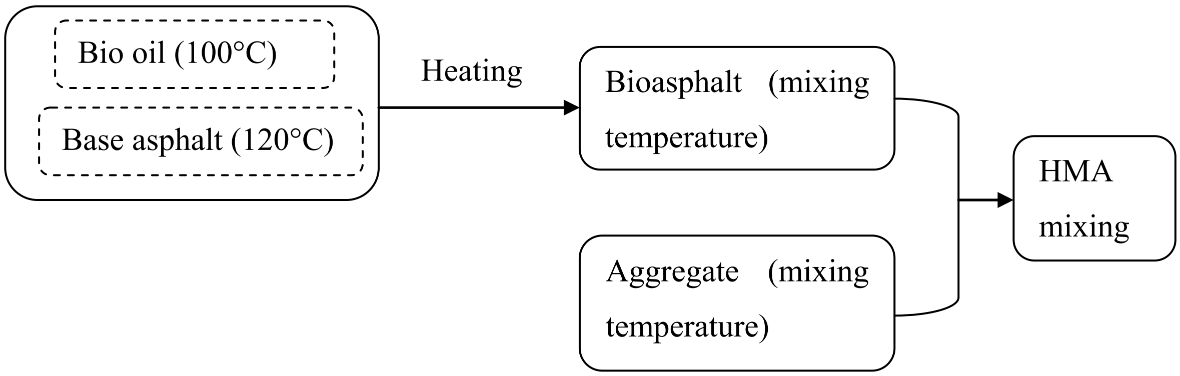


Figure 8-1: Flow chart for the HMA mixing

8.3 Current challenges and Future Efforts

In this study, the research team conducted a series of tests to evaluate the compatibility of bio oil and petroleum-based asphalt, the rheological roperties of bioasphalt and the mechanical performances of bioasphalt mixtures. Some findings were obtained based on the test results. However, the chemical mechanism during bio oil aging and how to simulate the short-term and long-term aging are the two main obstacles for the better use of bioasphalt.

Firstly, to reveal the inherent chemical mechanism of bio oil aging can present full explanation for the test results and further, to find ways to control the aging in a proper level. For instance, different chemical reactions that result in different rheological properties may occur at different temperatures. If these chemical reactions can be well understood, better ways to deal with the bioasphalt can be found.

Secondly, the standard RTFO and PAV aging are not suitable for bioasphalt, especially that with high percent of bio oil, because of the faster aging of bio oil. The short-term aging simulation can make guidance on the practical work of mixing and compaction. For example, the construction time and temperature should be reduced to avoid over aging of the bioasphalt. Theoretically, bioasphalt with different bio oil percentage should result in different construction time and temperatures to get the same aging level. Thus, to find a proper short-term aging method for bioasphalt would be very helpful for the design and construction of bioasphalt mixture. The long-term aging is dependent on the climate conditions of the pavement. The aging temperature for standard PAV test is 100°C. However, the actual high temperature for pavement is about 60 to 70°C, which is lower than the test temperature. The PAV test increased the aging temperature to accelerate the aging in a short time. However, this may be not suitable for bioasphalt because the aging increase of traditional asphalt from 60°C/70°C to 100°C may be lower than that of bioasphalt. In that case, the standard PAV test would over-estimate the long-term aging of bioasphalt. Thus, to find proper ways to simulate short-term and long-term aging for bioasphalt is very important for the application of bioasphalt.

The future direction for the research would be the design and practice for bio oil based asphalt mixture, especially for high percent bio oil containing asphalt mixtures. The mixture design should include: 1) bio oil percent selection and base asphalt selection; 2) aging level determination which can be adapted by changing the construction time and temperature; 3) short-term and long-term performance evaluation; 4) life cycle assessment.

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